1964

Effect of Submergence on Denitrification and Physicochemical Properties of Important Louisiana Soils.

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EFFECT OF SUBMERGENCE ON DENITRIFICATION AND PHYSICOCHEMICAL PROPERTIES OF IMPORTANT LOUISIANA SOILS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Agronomy

by
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August, 1964

ACKNOWLEDGEMENT

This work was partly made possible by a Hatch Act grant from the United States Department of Agriculture for which the author expresses his sincere gratitude. The author wishes to express his appreciation to his major professor, Dr. William H. Patrick, Jr. for his helpful suggestions and supervision throughout the course of his work. Appreciation is also extended to Messrs. R. H. Brupbacker and R. D. DeLaune for their technical assistance. Many thanks are also due to his parents, Mr. and Mrs. C. C. Redman, for their unfailing encouragement. Above all the author is grateful to his wife, Rita Louisa, and his daughter, Camila Marie, whose patience, understanding and inspiration have made this a reality.

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ABSTRACT

A laboratory study was conducted to determine the effect of submergence or waterlogging on denitrification and physicochemical properties of 26 Louisiana soils.

Nitrate reduction rates were determined using both a quantitative and a qualitative test for nitrate. The two methods were in general agreement. Nitrate reduction was directly correlated with clay and organic matter contents and the evolution of CO_2 and CH_4. Nitrate reduction rates were almost invariably increased by adding organic matter.

Denitrification was studied using the mass spectrometer for gas analysis. Nitrogen gas recovery from added nitrate ranged from 0.3 to 80.0%. Nitrogen was the only nitrogenous gas detected in appreciable amounts. All of the added nitrate was reduced by the soils.

Extractable ammonia was increased by submergence. Ammonia concentration was directly related to clay and organic matter contents. Additional organic matter resulted in an increase in ammonia production. With some soils this increase in ammonia was greater than the amount present as nitrogen in the added organic matter.

Extractable ferrous iron was increased markedly by submergence. Ferrous iron was directly correlated with clay and organic matter contents. The more acid soils had higher ferrous iron concentrations.

There was a direct correlation of ferrous iron with CO_2 and CH_4 evolutions. Additional organic matter tended to increase iron reduction.

Extractable phosphorus concentrations were increased an average of 21% by submergence. The organic matter content of the soil affected the amount of phosphorus released. Soils with ferrous iron concentrations after submergence of 1800 parts per million or less showed little or no increase in phosphorus extractability; soils which released higher amounts of ferrous iron released large amounts of phosphorus.

Extractable manganese increased approximately six-fold as a result of submergence. Added organic matter was not necessary for manganese reduction.

Soil pH before and after submergence was related. Soils with initial pH values below 7.4 increased approximately one-half pH unit per pH unit below 7.4; soils with initial pH values above 7.4 decreased approximately one-half pH unit per pH unit above 7.4. Increases in pH were attributed to hydrolysis of minerals and the increased solubility of reduction products. Decreases were probably due to organic acids and CO_2 production. The pH after submergence appeared to be buffered at around neutrality by some solid state substance, probably ferrous carbonate.

Increases in specific conductivity after submergence were directly related to clay, organic matter, ammonia, ferrous iron, phosphorus, CO_2 and CH_4 production. Soils with high initial nitrate concentrations

decreased in specific conductivity after submergence. Additional organic matter increased specific conductivity.

E_h measurements were conducted in special platinum electrode tubes. E_h and pH were inversely related immediately after flooding with an E_h - pH slope of -0.062 volts per pH unit. E_h values quickly dropped after flooding, and added organic matter accelerated this drop. The drop in E_h after submergence was retarded in those soils which released large amounts of iron. The reduction of iron oxide buffered the reduction process in the soil. E_h and pH were inversely correlated 30 days after submergence with an E_h - pH slope of -0.036 volts per pH unit.

CO_2 and CH_4 evolution measurements under waterlogged conditions were made with a mass spectrometer using special incubation jars. CO_2 and CH_4 were directly correlated with each other and with clay and organic matter contents. Generally, larger amounts of CO_2 than CH_4 were evolved from the flooded soils.

INTRODUCTION

Waterlogging of soils commonly occurs in Louisiana because of the fairly high rainfall and the poor surface and internal drainage of some soils. Other soils that are used for rice are intentionally flooded for a large part of the growing season. The physicochemical and biological changes that accompany waterlogging or submergence are important since they contribute to the suitability of the soil for crop production.

The properties of a waterlogged soil are substantially different from those of a well drained soil. In a well drained soil there is enough oxygen available from the atmosphere for microorganisms and higher plants. Flooding the soil changes this condition completely. Oxygen movement through the flood water is so slow that the soil no longer has a supply of oxygen. In the absence of oxygen facultative anaerobes and true anaerobes become active. Reduced organic and inorganic substances are produced. Many oxidation - reduction systems in the soil that are important to the nutrition of plants are affected by the anaerobic condition that results from waterlogging. Nitrate nitrogen present in the soil is subject to denitrification and loss from the soil. Organic matter decomposition is slower and less complete under anaerobic conditions. Nitrogen released through organic matter decomposition accumulates in the ammonium form since aerobic conditions are necessary for the microbial oxidation of ammonia to nitrate. Anaerobic conditions also result in the reduction of iron and

manganese compounds to more soluble forms. Phosphorus appears to be more available under reduced conditions. Soil pH is also influenced by submergence. The pH of reduced soils is generally higher and has a narrower range than the pH under well drained conditions.

This study was designed to measure the effect of waterlogging or submergence on several biological and physicochemical soil properities important to plant nutrition and growth. More specifically this study was designed to study:

(a) Nitrate reduction rates and denitrification under waterlogged or submerged conditions.

(b) Ammonia accumulation under submerged conditions.

(c) The accumulation of ferrous iron and manganous manganese in the soil under submerged conditions.

(d) The release of phosphorus from unavailable to available forms as a result of submergence.

(e) The effect of submergence on pH, redox potential and specific conductivity of the soil.

(f) The production of methane and carbon dioxide under waterlogged conditions.

(g) The interrelations of the various physicochemical and biological changes taking place as a result of submergence.

REVIEW OF LITERATURE

The chemical and physical properties of flooded soils are in many respects quite different from those of well drained soils. The following literature review makes an attempt to present in chronological sequence the research dealing with many significant physicochemical soil properties that are affected by submergence. These changes in physicochemical soil properties are closely related to concurrent biological changes.

The physicochemical and biological changes to be dealt with are: (a) nitrate reduction and denitrification, (b) ammonia accumulation, (c) iron reduction, (d) phosphorus release, (e) manganese reduction, (f) pH, (g) specific conductivity, (h) redox potential and (i) gas production.

Nitrate Reduction and Denitrification.

The literature on nitrate reduction and denitrification is extensive and often contradictory. Recently definite progress has been made with the use of the mass spectrometer and other advanced techniques for identifying and measuring gaseous products. Nitrate reduction usually appears under conditions of a limited oxygen supply. Nitrate serves as the hydrogen acceptor for some soil microorganisms in enzymatic dehydrogenation of the organic or inorganic substrate. Nitrate reduction in the latter sense has been called "denitrification" in order to distinguish this from the nitrate reduction in connection with nitrate assimilation as a nutrient by microorganisms. The

mechanism of denitrification is not fully understood. This process generally leads to gaseous reduction products of nitrate such as nitrous oxide (N_2O), nitric oxide, (NO), and molecular nitrogen, (N_2). Thus, denitrification causes a direct loss of plant-available nitrogen in the soil.

Fraps (1906) in dealing with rice soils in Texas stated that during flooding no nitrification took place but that reduction of nitrates or denitrification was indicated. Working in Hawaii, Kelly (1911) observed that swamping led to a considerable fall in the nitrate content and that nitrites formed were toxic to plants. Among early investigators Greaves and Carter (1920), in Utah, studied the influence of moisture on bacterial activities of the soil. They demonstrated the important role that microorganisms play in soil transformations. With regards to nitrate nitrogen they found that the quantity accumulating in the soil progressively increased with increasing water up to 60 per cent of the water-holding capacity.

Studies on waterlogged soils, from India and Rothamsted, by Subrahmanyan (1927) revealed a significant though only slight diminution in the nitrate nitrogen in ten days. The amounts lost had no relation to either the respective total nitrogen contents or amounts of nitrates originally present. Furthermore, there was no marked loss of ammonia by volatilization, nor any considerable variation in the nitrites so that the total nitrogen did not vary noticeably. Janssen and Metzger (1928) found that flooding rice soils resulted in a great reduction of the nitrates though the nitrite content never rose significantly.

Further work by Subrahmanyan (1929) indicated that in the absence of decomposing organic matter nitrogen was not lost when nitrates were added. There was, nevertheless, a rapid depletion of nitrates, when small quantities of fermentable matter, such as glucose, were added. This rapid disappearance of nitrates he attributed to transformation into other forms of nitrogen, namely, assimilation by microorganisms.

Prescott and Piper (1930) studied a south Australian soil with regards to nitrate fluctuations and found that beyond 70 per cent saturation conditions existed which were favorable for the disappearance of nitrates.

De and Sarkar (1936) added nitrates to waterlogged soils which they incubated and sampled up to 30 days. They found that under these conditions there was a rapid disappearance of nitrates. This loss of nitrate was not attributed to the reduction of nitrate to ammonia. There was also no evidence to show that nitrates were denitrified under these conditions. They presumed that nitrates were assimilated by microorganisms in the presence of an energy material. This view was supported when they obtained a rise in bacterial numbers and an increase carbon dioxide production.

Oxidation-reduction potential studies revealed to Pearsall and Mortimer (1939) that below a potential of 350 millivolts, approximately, corrected to pH 5, nitrates disappeared due to reduction and/or denitrification.

Work by Willis and Sturgis (1945), in Louisiana, attribute some nitrogen losses to changes in temperature and reaction in flooded soils. The quantities of nitrogen lost as ammonia at 100°F were large with

a high soil nitrogen content. The losses were comparatively small at 80 to 85°F with a low soil nitrogen content. Increased losses of nitrogen occurred with a decrease in hydrogen ion concentration. The net effect of these findings suggested that ammonium nitrogen in flooded soil water is unstable as a result of alkalinity and high temperatures, 85 to 107°F.

The total nitrogen content of soils remained virtually constant throughout the year in rice soils at Dacca, India, according to Bhuiyan (1949), but during the waterlogging period nitrates were absent.

Employing the use of isotopic nitrogen-15, Jones (1951) discarded the suggested mechanism of nitrogen loss by the Van Slyke reaction in which nitrates react with compounds such as ammonia or amino acids to liberate an equal amount of nitrogen gas for each of the reacting groups as follows:

$$RNH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2$$

Most of the nitrate lost he considered to be due to dentrifying bacteria that utilize the oxygen of these compounds to liberate nitrogen gas. Under anaerobic conditions 80 per cent of the added nitrogen was lost as nitrogen gas within three days. The rate and extent of loss was almost as great where no source of energy was supplied as where 0.5 per cent sucrose was added.

Denitrification was demonstrated under aerobic and partly anaerobic conditions by Broadbent (1951), in California. The soils under study all had less than 1.5 per cent organic carbon and denitrification took place even without added organic matter. Below 4.5 per cent oxygen, nitrates disappeared from untreated soils. There was

a lost of nitrogen at all oxygen levels when nitrate or ground clover was added. Only at the lowest oxygen level of 0.14 per cent was there a utilization of nitrate for oxidation of organic matter as evidenced by greater carbon dioxide production in the presence of nitrate. Broadbent contended that the rate of denitrification was more affected by the quantities of nitrate and oxidizable carbon in the soil than by the partial pressure of oxygen. Most nitrates were lost at pH 6.3. Furthermore, he suggested that a low oxygen concentration was not a necessary condition for the denitrification process, and that consequently the large losses of nitrogen from California soils were probably due to aerobic denitrification.

Jansson and Clark (1952) studied denitrification from the biological point of view. They found that for extensive denitrification from added nitrate a vigorous bacterial activity and an alkaline reaction were necessary. At an acid reaction bacteria were replaced by fungi and there were no appreciable losses of nitrogen. In an acid medium bacterial growth and biological denitrification were prevented by nitrite toxicity.

Broadbent and Stojanovic (1952) used nitrogen-15 tracer to confirm the importance of denitrification in the nitrogen cycle. Soil samples were incubated at oxygen concentrations of 0.1 per cent, 1.8 per cent, 4.2 per cent and 19.0 per cent. Some samples had 0.1 per cent peptone added as organic matter and some had none. The effect of the partial pressure of oxygen was that the amounts of nitrogen lost from the system, after treatment with nitrate salts, were inversely related to the oxygen content of the soil air. They

traced some loss of nitrate through denitrification even at 19.0 per cent oxygen.

Nitrogen-15 was also used as a tracer in a quantitative investigation on denitrification by Wijler and Delwiche (1954). The salient aspects of their investigation were that:

(a) Denitrification freed nitrous oxide, nitric oxide and nitrogen gas.

(b) Nitrous oxide was the major denitrification product, although under flooded conditions nitrogen was probably the major product.

(c) Denitrification was related to water content since increasing soil moisture increased denitrification by inhibiting diffusion of oxygen into the soil.

(d) Below pH 7 the reduction of nitrous oxide was strongly inhibited whilst above pH 7 nitrous oxide was readily reduced to nitrogen.

(e) Oxygen greatly suppressed the rate of denitrification.

(f) The initial nitrate concentration did not influence the rate of denitrification.

(g) The isotope content of all the denitrification products showed that they were all derived from nitrate indicating that non-enzymatic denitrification did not take place.

(h) Very little labelled nitrogen was present in the organic faction.

In a submerged soil, ammonia added to or formed in the upper soil layer (oxidizing zone) is oxidized to nitrite or nitrate which

then may pass on to the reducing zone below where it is there denitrified to elemental nitrogen. It follows, therefore, that if a nitrogenous ammounium fertilizer be directly applied to the reducing zone there should be no loss of nitrogen. Even so, De and Digar (1955), working on rice soils, revealed nitrogen losses when ammonium sulfate was applied to a depth of three inches below the soil surface. Oxidation of ammonium sulfate apparently took place even at this depth. Further evidence of this relatively deep oxidizing zone was the absence of hydrogen and methane in the gas mixtures from this depth. This implied that these gases were oxidized to water and carbon dioxide, respectively, in the course of their movement through this oxidizing zone.

Results by Patrick and Sturgis (1955) indicated that there was little change in oxygen concentration from the surface of the flood water down to the soil but once the surface of the soil was reached the oxygen content decreased very rapidly so that there was no oxygen present one centimeter below the soil-water interface. The above investigators also found that submergence increased the rate of reduction of oxygen, and that the addition of organic matter had a further increasing effect. The Crowley silt loam soil they studied showed a marked decrease in added nitrate nitrogen from 20 parts per million to 0.1 - 0.2 parts per million within 30 days after the first addition.

Denitrification tests using labelled nitrogen-15 were carried out by Nommik (1956). He concluded that below 60-70 per cent of the water-holding capacity there was no, or negligible denitrification. At 3°C there was no denitrification and at 60-70°C denitrification was

greatest. Low pH values inhibited denitrification while high values promoted this. Nitrate concentrations did not affect denitrification but denitrification was directly correlated with the partial pressure of oxygen at low soil moistures. High nitrate and nitrite concentrations promoted the formation of nitrous oxide and nitric oxide respectively.

Hauck and Melsted (1956) accounted for 89-100 per cent of the total nitrogen in a closed system when nitrate nitrogen, labelled with nitrogen-15, was added to wet soils. These workers used the mass spectrometer, and the infra-red spectrometer to determine the production of nitrogen gas and nitrogen oxides. They encountered an abundance of nitrous oxide evolved from wet soils, especially at pH values less than 6.0. Limed soils reduced twice as much nitrate nitrogen to gaseous forms of nitrogen, after four days incubation, as compared to unlimed soils.

Andrews and Singh (1957) emphasized the importance of denitrification in fertilization following wet periods on heavy soils. Using a Houston clay soil denitrification losses were 25 pounds of nitrogen per acre per week at 4°C, the rate increasing with each increase in temperature and at 28°C the loss was about 37.5 pounds per acre per week. A highly significant correlation existed between nitrogen lost by denitrification and carbon dioxide produced in 96 hours which was considered a measure of the readily decomposable organic matter.

Working in Japan, Yamane (1957) reported that in flooded soils the amount of gaseous nitrogen evolved corresponded closely to the loss of nitrate nitrogen.

According to Loewenstein et al. (1957) large volatile losses of nitrogen occurred from uncropped soils at field moisture levels. Their study signified that denitrification and nitrification proceeded simultaneously in the soils. Evidently, nitrates produced in the aerobic soil area moved to oxygen-poor regions and became subject to denitrification. They suggest the possibility that an aerobic area may become anaerobic as a result of rapid oxygen consumption or because of concurrent carbon dioxide evolution by the soil microflora thereby leading to denitrification.

Bremner and Shaw (1958), at Rothamsted, substantiated the findings of a number of previous workers while investigating the factors affecting denitrification. Their data showed that:

(a) Rapid denitrification of nitrate was induced by incubating the soil under waterlogged conditions with organic materials such as glucose.

(b) The percentage of added nitrate nitrogen lost by denitrification on incubation of waterlogged soils with sufficient glucose was the same whatever the level of application of nitrate nitrogen.

(c) Denitrification was accompanied by a rapid but temporary accumulation of nitrite and the formation of smaller amounts of ammonia.

(d) Under conditions conducive to denitrification, 80-86 per cent of the nitrate nitrogen added to the soil was lost in five days.

(e) The rate of denitrification was very slow at a pH less than

4.8, increased with rise in soil pH, and was very rapid at pH 8.0-8.6.

(f) The rate of denitrification increased rapidly with a rise in temperature with an optimum temperature at about 60°C.

(g) Below about 60 per cent of the water-holding capacity of the soil no denitrification occurred, above this level it increased rapidly with increase in moisture.

(h) Denitrification in soil depended on the amount and type of organic material present and occurred only when the supply of oxygen required by the microorganisms was restricted.

Denitrification in three variously treated well aerated soils was investigated by Carter and Allison (1960). The extent of loss of nitrogen was determined by the differences in total nitrogen and excess nitrogen-15 before and after incubation. Very little, if any, nitrogen loss occurred under aerobic conditions except where dextrose was added in the presence of nitrate. The losses of nitrogen-15 under these conditions commonly varied between zero and 12 per cent. Wheat straw additions produced no significant losses. Additions of calcium carbonate also had no significant effect on nitrogen losses considering that initially the soils' pH varied between 5.4 and 5.8. They concluded that denitrification was of minor importance in soils that are strictly aerobic although the authors noted that this ideal condition may not exist at all times even in open soils.

Allison, Carter and Sterling (1960) also used nitrogen-15 to study denitrification under varying partial pressures. In a sandy soil at one-third atmosphere moisture content (field capacity) there

was no denitrification both in the absence and in the presence of 1 per cent glucose or 2 per cent wheat straw. At 2.27 per cent oxygen significant losses of nitrogen occurred in some samples. At 0.46 per cent oxygen nitrogen losses were 10 per cent in the absence of an energy source and 50 per cent in the presence of 0.5 per cent glucose. They concluded that denitrification may at times be expected in open and well drained soils.

In following the products of anaerobic denitrification Cady and Bartholomew (1960) found the following sequence through mass spectometer analyses: First nitric oxide appeared, secondly nitrous oxide appeared and increased and coincidently nitric oxide disappeared, thirdly nitrogen gas appeared and this increased in amount sufficient to account for 83 to 95 per cent of the added tagged nitrate coincident with the reduction in amount and eventual disappearance of nitrous oxide.

Nitrate reduction rates in relation to controlled redox potentials were studied by Patrick (1960). There was a decrease in the nitrate content at potentials less than 338 millivolts. When the redox potential was decreased there was an evident increase in the rate of nitrate nitrogen reduction. The nitrate concentrations did not affect the reduction rate as illustrated by the linear nature of the nitrate concentration-time curve. This non-dependence of denitrification on the soil's nitrate concentration collaborated with results obtained by other workers.

The effect of oxygen on "aerobic denitrification" was studied using nitrogen-15 tagged nitrate as a tracer material by Cady and

Bartholomew (1961). Soil samples were incubated in a laboratory apparatus constructed to maintain constant partial pressures of oxygen. Periodic analyses of the gaseous phase were made on a mass spectrometer. A marked effect of oxygen on the rate of denitrification was exhibited. Both atmospheric oxygen and combined oxygen (nitrate) were utilized but the decrease gaseous loss of nitrogen at the higher levels of free oxygen disclosed a preferential use of the former. Their studies showed that only under conditions of high levels of carbonaceous material, an available nitrate supply, and an oxygen level less than 7 per cent by volume would an appreciable amount of nitrate be reduced to gaseous forms.

Ammonia Accumulation

Arable soils, especially if they are not too acid, have a low content of ammonium nitrogen. On the other hand a high content of ammonium nitrogen is characteristic of submerged soils. The ammonia that appears after submergence comes from mineralization of part of the organic fraction. The biological oxidation of ammonium nitrogen to nitrate nitrogen that occurs in well drained soils is inhibited by the anaerobic conditions of submerged soils.

One of the earliest investigations concerning ammonium nitrogen accumulation in rice soils was undertaken by Fraps (1906) in Texas. His data showed a definite production of ammonia under 100 per cent moisture saturation capacity. His data also showed that ammonia production in flooded soils was less than under cultivated condition, with less moisture.

Russell and Hutchinson (1909) furnished proof that the production

of ammonia was mainly the work of microorganisms. They considered that the curves of ammonia accumulation belonged to the type associated with bacterial rather than purely chemical changes--they were sigmoidal in shape. Also, partially sterilizing the soils, by heating to 125°C, made them behave altogether differently in that there was no accumulation of ammonia during incubation. Finally, if toluene was left in the soil there was only a slow production of ammonia and never a rapid rate, the curve was more nearly linear. The action of microorganisms was here excluded but enzymes may have acted. Panganiban (1925) reported that ammonification took place between 15°C and 60°C, with faster rates at higher temperatures. Murphy (1926) stated that: "Ammonification studies are important at least from one stand point, namely, that of showing the rate of decomposition of the crude organic nitrogenous materials into a more available form of nitrogen for plant use."

In a thorough study on the effects of waterlogging on nitrogen compounds, by Subrahmanyan (1927), a very distinct increase in free and saline ammonia content was observed even at the end of the first 24 hours. This increase continued up to the seventh day before leveling off. There was no correlation whatever between the rate of ammonia production and the total nitrogen content or the amount of ammonia originally present in the soil. This study led Subrahmanyan to suggest that the formation of ammonia was due to an enzyme and not entirely to biological action on the evidence that the production of ammonia took place even in the presence of volatile antiseptics. He ascribed the presence of diaminase in waterlogged soils to its role in the production of ammonia.

In Arkansas, Janssen and Metzger (1928) found that submerged rice soils showed a steady increase, over a two month period, from 4.1 parts per million to 34.0 parts per million of ammonia when green manure was applied.

According to Screenivasan and Subrahmanyan (1935), Joachim and Kandiah (1929), in Ceylon, noticed that when green manures were plowed under immediately before flooding large quantities of ammonia were found and they therefore recommended green manuring of paddy fields in the puddled state because the ammonia released was assimilated by the crop.

In agreement with the findings of Joachim and Kandiah, Bartholomew (1929), in Arkansas, highly recommended organic forms of nitrogen. He observed good results from use of these forms.

Screenivasan and Subrahmanyan (1935) detected ammonia as the chief form of mineralized nitrogen in waterlogged soils. Their results suggested that the chief factor determining the efficiency of mineralization of nitrogen is the ratio of carbon to nitrogen. Materials with narrow ratios mineralized very much more rapidly than those with wide ratios. The quantities of ammonia present in the medium increased up to a point, after which there was a steady decrease but no reason was given for this decline. Their experiments illustrated that under swamp conditions ammonification proceeded at a very much faster rate than nitrification so that there was an accumulation of ammonia in the medium.

De and Sarkar (1936) could not attribute loss of nitrate to be due to its reduction to ammonia. They reported an initial rise in the ammonia content of flooded soils soon after waterlogging, the concentration reached a maximum in about six weeks, remained stationary

for about one month, and then fell. This loss of ammonia, after an initial rise, they pointed out as being in accord with some of their previous findings.

Ammonification has been studied from the view point of it being a photochemical reaction. Rao and Varadanam (1938) found the decomposition of various nitrogenous compounds to be a purely photochemical reaction in the presence of photocatalyst, like heated soil or ignited ferric oxide. Singh and Nair (1939), in India, concluded that biological reactions were largely responsible for the process of ammonification in soil, though they found nitrite to be formed as a result of photochemical action.

Bhuiyan (1949) presented quantitative data on the amounts and transformation of different forms of nitrogen in rice soils. He confirmed previous investigations as to the rapid rise in ammonia after the soil had been waterlogged, reaching a maximum, and thereafter decreasing to a fairly constant level.

Owen, Winsor and Long (1950) found a highly significant correlation between carbon-nitrogen ratio and the formation of both ammonia and nitrate nitrogen from a series of amino acids added to the soil. There was a greater percentage recovery of added nitrogen the narrower the carbon-nitrogen ratio.

Broadbent and Stojanovic (1952) could not detect any reduction of nitrate to ammonia using nitrogen-15 as a tracer when two different loam soils were incubated under various oxygen levels ranging from 0.1 to 1.9 per cent.

Mitsui (1954) described an experiment which illustrated the

relationship between the carbon-nitrogen ratio and mineralization. He pointed out that the accumulation of ammonium nitrogen under waterlogged conditions without exception obeyed the order of the carbon-nitrogen ratio of the soil in a 34 day incubation period, at 26°C. The largest accumulation of ammonium nitrogen occurred with the material added with the narrowest carbon-nitrogen ratio. Due to repeated decomposition by soil microbes, samples with wide carbon-nitrogen ratios showed an accumulation of ammonium-nitrogen in the latter half of the incubation period, that is to say, after 34 days. Under these waterlogged conditions the mineralization curve showed a maximum of ammonium nitrogen accumulation, and then a decline with an extended incubation period. Generally speaking, organic materials having wider carbon-nitrogen ratios than 20 will take up mineral nitrogen from the soil while if the carbon-nitrogen ratio remains under 15 some of the nitrogen of the organic material will be converted into mineral nitrogen during the earlier period of incubation. Relative to all of this is the reason why in the tropics green manures with a carbon-nitrogen ratio of about ten are frequently reported as efficacious as ammonium sulfate in producing rice.

Wijler and Delwiche (1954) studied denitrification quantitatively using potassium nitrate labelled with nitrogen-15 as a tracer and could detect very little reduction of nitrate to ammonia even when all the nitrate was lost during denitrification. Nitrate was reduced to ammonia in large amounts only when excessive amounts of organic matter were added under anaerobic conditions.

Harmsen and Van Scheven (1955) have reviewed the literature

pertaining to organic nitrogen mineralization. They pointed out that under the waterlogged and anerobic conditions existing in rice soils ammonification (the decomposition of organic compounds of nitrogen into ammonia) proceeds almost normally.

Iron Reduction.

In most arable soils virtually all of the iron remains in the oxidized condition. When anaerobic conditions are established in soils by waterlogging, a considerable amount of reduced iron may accumulate. This reduction has been studied from many points of view. Today most of the literature revolves around the fact that the process is affected by the activities of microorganisms in the soil who utilize the ferric iron as the terminal electron acdeptor to oxidize the substrate. Non-biological reduction of iron has also been proposed.

Starkey and Halvorson (1927) and Halvorson (1931) discovered that under anaerobic conditions, in dextrose or peptone media, microorganisms could dissolve and reduce iron as a result of decreasing the oxygen pressure. Organic compounds of iron may form subsequent to solution of iron in organic media. Upon atmospheric exposure of solutions containing iron dissolved and reduced under anaerobic conditions, oxidation took place and precipitation occurred. These latter changes were thought to be independent of microbial activity.

Submerged soils have a high iron content according to Robinson (1930). This high concentration of iron he attributed to carbon dioxide produced as a result of microbial action on organic matter. The carbon dioxide was thought to be responsible for holding the iron

in solution. Shortly after flooding, submerged soils developed high concentrations of ferrous iron. In the absence of organic matter the solubility of iron was not increased under submerged soil conditions.

Kliman's study (1937) seemed to point to the utilization by the plant of ferrous iron when it is present in the cationic form. In higher plants iron is transported as the ferrous ion in the phloem and remains in this state.

Oxidation-reduction potentials studies carried out by Pearsall and Mortimer (1939) showed that ferrous iron disappeared above a potential of approximately 350 millivolts, at pH 5. In natural waters, ferrous iron was only detectable below this potential.

Ignatieff (1941) investigated Canadian soils and found well drained soils to contain very small quantities of ferrous iron, sometimes none. Under waterlogged conditions large quantities of ferrous iron were produced rapidly, after an initial lag of two to three days. The soil ferrous iron was not readily brought into solution by water, but by the use of salts the ferrous iron could be displaced from the soil. This indicated that ferrous iron entered into the base exchange complex of the soil. Under anaerobic conditions soil water could bring into solution quantities of ferrous iron, but much larger amounts of this ion were held on the soil base exchange complex. This reduction of iron he attributed mainly to biological processes.

The work of Somers and Shive (1942) indicated a definite interrelation in the metabolic functions of iron and manganese. Iron-manganese ratio values above two invariably produced a specific type of chlorosis resulting from excess iron, or deficient manganese, or

both. Ratio values much below this effective range invariably produced a specific chlorosis of a different type resulting from excess manganese, or deficient iron, or both.

Confirming the above, Twyman (1946) stressed the importance of the iron-manganese balance both in the plant itself and in the substrate in which it grows. The incidence of pathological symptoms of manganese and iron deficiency seems to be governed by the relative proportions of these elements.

Results by Hester and Skelton (1947) showed that considerable ferric iron was in solution in a submerged soil with even larger amounts of ferrous iron being present. The top soil of 24 Canadian soils when submerged contained on the average more soluble iron than the subsoil. The breakdown of organic matter was obviously influencing the solubility of iron.

Fujiwara (1950) had observed the surface layer of paddy soils to be high in ferric iron. This layer is oxidized under flooded conditions by oxygen in the irrigation water. In the underlying layer, which is under reduced conditions since oxygen is consumed faster than it could be replenished ferrous iron was present.

Pearsall (1950) stated that: ". . . soils in the reducing state liberate larger amounts of exchangeable cations". Particularly high in concentration of the cations liberated is iron. According to Bloomfield (1953) ferric iron can be indirectly reduced by products of microbial decomposition of organic matter. He demonstrated this non-biological reduction of iron using aqueous extracts of pine needles.

The release of available phosphorus due to the reversion of ferric iron to ferrous iron was studied by Islam and Elahi (1954).

They found that the addition of oxidizable substances increased this transformation. It was also pointed out that this may either be chemical or biological, although they presumed it to be mostly chemical.

Bromfield (1954) isolated bacteria that could reduce ferric compounds. These organisms were unable to derive oxygen for their growth from ferric oxide under anaerobic conditions, but when another compound containing available oxygen was supplied, growth and reduction of ferric compounds occurred.

A study by Lutwick and DeLong (1954) showed that natural rainfall leachates from decomposing leaves had the capacity to mobilize iron. Comparative data to the same effect is also presented by Schnitzer and DeLong (1954) who found that laboratory prepared leaf extracts also had the capacity to mobilize iron.

Ponnamperuma (1955) found that submergence of a soil caused a tremendous increase in the concentration of soluble iron. The concentration of ferrous iron was affected by pH under anaerobic conditions, being higher at lower pH values. The addition of oat straw to waterlogged soils had the effect of increasing the concentration of iron, this was most marked in the early stages of flooding, up to approximately 60 days.

Clark and Resnicky (1956) treated a silty clay loam soil with finely ground rice straw at the following rates: 0, 0.1, 0.2, 0.4, 0.8, and 1.6 per cent. These samples were flooded, incubated at 26.5°C and periodically sampled up to 105 days. Rate-time effect data showed that up to 35 days iron contents were directly related to the rate of straw addition. By this date, a peak value had been reached in the

1.6 per cent straw treatment. Peak values were not reached until the 84th day in treatments receiving lesser amounts of straw.

Experiments conducted in the laboratory by Islam and Chandhury (1960), in India, showed that after two months of waterlogging soil samples the iron concentration had increased at the surface and decreased at lower depths. A striking feature of this experiment was that for all depths the iron concentration had increased on the bright side of the incubation cylinder. The accumulation of iron at the surface was explained by the fact that soluble ferrous iron moved towards the surface and there became converted to relatively insoluble ferric iron. The higher concentration of iron on the bright side of the cylinder may have been due to the effect of photochemical reactions or the oxidation of ferrous iron by oxygen liberated by the algae growing on the bright sides of the cylinders. It was assumed that such a phenomenon also occurs in the paddy field.

Mandal (1961) conducted pot experiments with rice grown in waterlogged soils with and without the addition of organic matter. By means of soil and drainage water analyses he found that when no organic matter was added there was at the start a sharp rise in insoluble ferrous iron. Later ferrous iron entered in the exchange complex as the carbon dioxide increased. Still later, with a further increase in carbon dioxide ferrous iron appeared in the drainage water. The addition of organic matter intensified the reduction process, produced more carbon dioxide and consequently the insoluble, exchangeable and soluble ferrous fractions appeared more rapidly and in larger amounts than when no organic matter was added.

In a later study, Mandal (1962) found that the concentration of iron in the drainage water from flooded rice soils was highest in the soils which had an oxygen content of 10 per cent in the soil solution. This coincided with the highest absorption of iron and the highest dry weight yield.

Ng and Bloomfield (1962) reported that the presence of organic material increased the amount of iron extracted with water and neutral ammonium acetate when a soil was submerged. Immobilization resulted upon subsequent aeration, and although drying further decreased the amount of iron extracted, the net result of flooding and drying was to increase the extractability of iron.

Kamura et al. (1963) have recently proven that the mechanism of ferric iron reduction in paddy soils is entirely affected by the activities of microorganisms in the soil.

Takai et al. (1963) noted a direct relationship between the amounts of ferrous iron produced in submerged soils with the amount of free iron content in the soil. These workers further noted that the ferrous iron content in the soil, E_h (redox potential) and pH were closely connected with each other, suggesting that E_h and pH of the submerged soil are greatly influenced by the amount of ferrous iron.

Patrick (1964) studied the extractable iron in a waterlogged Crowley silt loam soil under conditions of controlled redox potential. The results indicate that when the redox potential fell below +200 millivolts, there was a very large release of ferrous iron. The greater the decrease below +200 millivolts, the greater the release of

iron. A straight line function related the ferrous iron concentration between the potentials of -200 millivolts and +200 millivolts. The high concentration of ferrous iron was due to the reduction of insoluble ferric compounds which were unstable at reducing potentials.

Changes in Extractable Phosphorus.

It has been observed for a long time that the response to phosphorus fertilization in rice soils of the United States as well as in other parts of the world, has been radically different from that of well drained soils. This phenomenon is of utmost practical significance in rice fertilization.

Bartholomew (1928), reported that: "Phosphatic fertilizers for rice have not as a rule, in Arkansas, proven profitable even though irrigated crops on the same field have given increased yields when fertilized with superphosphate (acid phosphate)."

Bartholomew (1931) studied this lack of response to phosphatic fertilization still further. At that time the hypothesis commonly offered by rice growers to explain the condition mentioned, was that phosphatic fertilizers stimulated weed growth to such an extent that the weeds could not be controlled by irrigation. As a consequence, a considerable amount of plant nutrients were used up by the weeds and no increase yields of rice were obtained. Bartholomew contended that the irrigation water had considerable amounts of calcium which could cause phosphorus in the soils to revert to insoluble forms. Also, the development of anaerobic conditions after irrigation might have caused some of the available phosphorus to be

changed to forms unavailable to rice. His findings showed irrigation to cause a decrease in water-soluble inorganic phosphate. This was partially due to reversion of the phosphates. There was also an increase in the organic water-soluble phosphorus three months after irrigation ascribed to bacterial activities under anaerobic conditions. The recommendation on the basis of the interpretations given to the results was that phosphatic fertilizers should not be used when calcareous water was to be used for irrigation.

Kapp (1933) cites work by Nagaoka (1904) who reports that larger increases in yields of rice were obtained by applying ferric, ferrous, aluminum, and calcium phosphates when compared with acid phosphate. Kapp's results showed that phosphorus added to two Arkansas silt loam rice soils under greenhouse conditions did not, in all cases, increase the yield of rice. The soil solution contained a very small amount of available phosphorus. Large additions of slaked lime, 10,000 pounds per acre per two years, did not decrease the phosphorus content nor the growth of plants when compared with untreated plots.

The process of phosphorus mineralization is definitely important, particularly in soils high in organic matter, as emphasized by Pearson et al. (1941). These investigators added various materials containing organic phosphorus to 100 grams of limed and unlimed samples of a fine sandy loam soil which was incubated at 25°C with 16.5 per cent moisture for 60 days. In all cases the addition of lime caused an increase in the amount of dilute acid-soluble inorganic phosphorus due to more rapid mineralization and increased solubility of inorganic phosphorus compounds in the soil.

Glentworth (1947) studied the same Scottish soil under a naturally free drainage condition and under an impeded drainage condition with regards to the distribution of phosphorus in its profile. The results pointed to a loss of phosphate in the ground water from the latter condition. Similar results to these were reported by Glentworth and Dion (1949) as illustrated by the relative amounts of phosphorus in two contrasted profiles of the same field, as given below:

	Freely Drained	Poorly Drained
Horizon A	100	78
Horizon B	73	42
Horizon C	64	42

According to Paul and DeLong (1949), Hardy and Rodrigues (1946), in Trinidad, suggested a downward movement of phosphorus to have occurred in British Guiana soils, particularly in flood-fallowed soils. Data by the former workers with a heavy textured Canadian soil, which was flooded using a free-drainage and a stagnant method with and without 1.0 per cent glucose, suggested a downward movement of the easily-soluble inorganic (Truog)phosphorus, especially in a soil-glucose solution system. Data also indicated a definite accumulation of easily soluble organic phosphorus. After air-drying the values of organic phosphorus were definitely lower than those of the moist soil at the end of the flooding period, but these were still about three times as great as was extractable from the original dry soil. The values of inorganic phosphorus were lower than those from the wet soils at the end of the flooding period and lower than those in

the original dry soil. These results were explained as being due to biological reduction of iron during the flooding phase, followed by re-oxidation during the desiccation phase. The net result of this phenomenon was an increase in the phosphorus fixing capacity of the sesquioxidic fraction.

The fact that in flooded rice fields there is a surface layer rich in oxygen (oxidizing zone) and an underlying, oxygen-deficient layer, where oxygen is consumed by decomposition of organic matter (reducing zone) led Fujiwara (1950) to conclude that in the reduced zone ferric phosphate is reduced to the more soluble ferrous phosphate form and thereby greatly improved its manurial value. Fujiwara further noted that when water was removed, as in winter, oxidation of the ferric salts occurred and the efficacy lower. Since aluminum phosphate is not reduced in paddy condition its manurial value for paddy rice is slightly inferior to iron salts, but owing to the waterlogged condition hydrolysis goes on and increases its effect.

On the basis of plant uptake, Dalton et al. (1952) found that when organic matter was added to soil as an amendment it effectively increased the availability of soil phosphate. Easily decomposable organic matter was more effective in this regard than organic substances that decomposed slowly.

McGeorge (1953) found that when superphosphate was applied to a poorly drained soil the increase in available phosphate (extracted with 0.5 normal acetic acid) content of the soil was greater, and of longer duration, than when a similar dressing was applied to a freely drained soil. Fixation of phosphate appeared to be less rapid

and less complete under poor drainage conditions. Applying superphosphate to a poorly drained soil resulted in increases in "available" phosphate down to a depth of seven inches or more, but, in a freely drained soil increases of "available" phosphate were not registered below three to four inches. Downward movement of total phosphate (digested with concentrated sulfuric acid and nitric acid) was appreciable in poorly drained soils. It was concluded that losses of top-dressed phosphate from surface layers of poorly drained soils are important. In the freely drained soils, however, nearly all the applied phosphate was retained in the top three to four inches.

Mitsui's explanation (1954) for the remarkably different behavior of phosphate in paddy soil and upland soil is based on the higher solubility of ferrous phosphate as compared to ferric phosphate. He reported that the solubility, in flooded conditions, of phosphate increased greatly above pH 4.5 and below pH 7.0.

Ponnamperuna (1955) was able to confirm the theoretical predictions of other investigators, and their practical observations, in that the solubility of phosphate increased on submergence and reduction of a soil.

The findings of Gasser (1956) are also in agreement with effects noted by other workers, particularly the increase in dilute acid-soluble phosphate occurring on waterlogging acid soils attributed to the reduction of ferric phosphate.

Shapiro (1958a) noted that flooding increased the availability of soil phosphorus, yield, and phosphorus uptake by rice plants. Shapiro (1958b) also noted that the addition of spent brewer's hops to a flooded soil increased the availability of both inorganic and organic

phosphorus. He showed that reduction was the most important factor in phosphorus availability.

Islam and Elahi (1960) have confirmed the reversion of ferric iron to ferrous iron under waterlogged conditions and attributed the greater availability of phosphorus under these conditions to the reduction of ferric phosphate. Their results clearly showed that waterlogging alone increased the amounts of ferrous iron and readily soluble phosphorus. Moreover, the addition of oxidizable substances increased this transformation of ferric salts and thus increased the amount of readily soluble phosphorus. The greater amount of transformation was completed within three weeks' time. The nature of the transformation was attributed to either chemical or biological action though this was undetermined.

Most recently Patrick (1964), working with controlled redox potentials, found a definite relationship between extractable phosphate phosphorus and the redox potential of the soil. His data indicated a marked increase in extractable phosphorus when the redox potential fell below +200 millivolts. This phosphorus increased from 10 parts per million to 35 parts per million between the potentials of +200 and -200 millivolts. The fact that at +200 millivolts ferric iron also began to be reduced to ferrous iron tends to confirm that this increase in phosphorus came from the conversion of ferric phosphate to the more soluble ferrous phosphate.

Manganese Reduction

In well drained soils manganese is mostly present as the more oxidized and insoluble manganese dioxide (MnO_2). In flooded soils

the manganese dioxide is reduced to the less oxidized and more soluble manganous form in which form it can occur in large amounts. Manganese plays an important role in plant nutrition. The rice plant requires large quantities of this minor element.

Kelly and McGeorge (1913) disclosed data showing that the solubility of manganese in Hawaiian soils increased with time under reducing (wet) conditions. Conner (1918) found significant increases in the amount of replaceable manganese on flooding a soil.

Schollenberger (1928) found that when a one to one dry soil to water mixture was incubated, after three weeks, there was a very large increase in exchangeable manganese. The presence of 1.0 per cent starch heightened this effect. This was thought to be due to reduction of the higher oxides of manganese by bacteria. A consequence of this was that manganese oxides in the soil reduce and supply an active base with a decrease in acid reaction.

Metzger (1930) found that replaceable manganese increased upon flooding. He noted that in a twenty-year-old rice field the replaceable manganese was also significantly higher than in an adjoining non-irrigated field.

Findings by Robinson (1930) on submerged soils were that:

(a) The solubility of manganese increased with time of submergence where there was an appreciable quantity of manganese in the soil.

(b) The increase in manganese concentration was caused indirectly by the microbial action on the organic matter which produced carbon dioxide along with other

gases. It was the carbon dioxide thus produced that mainly held the manganese in solution.

(c) Organic matter greatly influenced the solubility of manganese under submerged soil conditions.

Piper (1931) waterlogged alkaline Australian soils with and without 0.25 per cent dextrose. Waterlogging increased the amount of water-soluble manganese more when additions of dextrose were made. This was associated with the greater bacterial activity of these soils, since anaerobic conditions developed sooner and became more pronounced than in the soils to which no dextrose had been added. Such reducing conditions were considered favorable to the reduction of manganese dioxide to soluble manganous compounds.

Somers and Shive (1942) established the interrelationship in metabolic functions between iron and manganese. Accordingly, symptoms of iron toxicity corresponded to those of manganese deficiency and vice versa. This was later supported in a review by Twyman (1946).

Results by Mann and Quastel (1946) clearly showed that manganese in soils underwent a metabolic cycle, the kinetics of which were determined by the nature of the microorganisms and the organic matter present.

Leeper (1947) noted that the higher oxides of manganese are reduced either by direct action with organic matter or by biological processes. Reduction by organic matter was more likely at low pH values, since the oxidizing power of the higher oxides increases rapidly with acidity. He noted that biological reduction could

take place at any pH value if the oxygen tension were low, at which time the anaerobic bacteria use the higher oxides as a source of oxygen.

According to Fujimoto and Sherman (1948), organic matter with a high carbon-nitrogen ratio increased the availability of manganese in the soil to a greater value. Organic matter with a high carbon-nitrogen ratio contains large amounts of easily oxidizable substances such as starch and sugar which when added to the soil are oxidized biologically with the formation of carbon dioxide.

Hurwitz (1948) could not detect any increase in exchangeable manganese in a soil incubated at 20 per cent moisture without added organic matter. The addition of soluble glucose and peptone increased microbial activity and increased the exchangeable manganese. The increase in manganese was considered due to a drop in redox potential.

Reduced soils liberate large amounts of exchangeable manganese according to Pearsall (1950).

Ponnamperuma (1955) observed identical changes for soluble manganese as for iron. The highest concentration of soluble manganese was associated with submerged, low pH treatments to which organic matter (oat straw) was added. He concluded that manganese was very easily reduced and it is only because of the low manganese content of soils that submerged soils do not attain even higher concentrations.

Clark and Resnicky (1956) showed some striking effects which length of flooding and the addition of organic matter have on the

increase in manganese. By 84 days the manganese concentration for the treatment receiving no additional organic matter actually exceeded the concentration for the 1.6 per cent treatment which suggest that the reduction process had "spent itself out."

Clark et al. (1957) observed a marked yield response to manganese by rice under flooded conditions. They concluded that rice had a high requirement for and an exceptionally high tolerance for manganese.

Islam and Choudhury (1960) conducted experiments in the laboratory which showed that after two months of waterlogging soil samples a redistribution of manganese had taken place. At the start manganese was uniformly distributed through the entire soil depth while under waterlogged conditions its concentration increased at the surface, as in iron.

Iron and manganese transformation in waterlogged rice soils were studied by Mandal (1961). This work indicated a somewhat different course of transformation of manganese from that of iron. Manganese entered into the exchangeable complex and also appeared in soluble form much earlier than iron. The reducible manganese, comprising higher oxides such as MnO_2, Mn_2O_3, and Mn_3O_4, showed a decrease for some time after the soil had been waterlogged and then began to increase to a level that was higher than at the start.

In a subsequent study, Mandal (1962) related the better growth of rice plants grown in soils which were under an atmosphere containing 10 per cent oxygen, to the beneficial effect of iron and manganese. Plants of this treatment absorbed the greatest amounts of iron and

manganese, had the highest dry weight, and the drainage water was highest in iron and manganese concentrations.

Changes in pH

A characteristic feature of waterlogged soils is that they are never very acid even though they may be base deficient. When these highly reduced soils are dried they usually become more acid. At the turn of the 20th century it was believed that poor drainage resulted in "sourness" of soils which was associated with an injurious degree of "acidity". In this respect correlations had sometimes been found between poor drainage and high lime requirements. Among the earliest references to this effect is that of Conner (1917) who investigated soils from tiled and untiled land and found that the drained soil required less lime than the undrained soil. A subsequent study was conducted by Conner (1918), on five Indiana soils, to investigate the effect of moisture on soil acidity. Acidity was determined by three lime requirement methods. The data clearly illustrated that there was a general marked decrease in acidity with increase in moisture contents. Even so, it was stated that: "The acidity of soils kept saturated with water for a period of time tended to decrease".

Gillespie (1920) first pointed out that waterlogging tended to make soils less intensely acid. He had found that the better drained soils had a higher hydrogen ion concentration than the more poorly drained soils. He believed that the so-called "sourness" of soils included something beyond acidity, probably the effect of a high state or reduction.

Subrahmanyan (1927) noted a distinct rise in the pH values as a result of waterlogging, principally during the early stages of waterlogging. A Rothamsted soil increased from pH 7.5 to pH 8.2 in seven days and an Indian soil, from Coimbatore, increased from pH 7.4 to pH 7.8 in four days. There was a slight decrease after that time, although the figures still remained higher than at the beginning. He also observed that the rise in the pH value was positively correlated with the logarithms of the corresponding amounts of free and saline ammonia.

In flooded rice soils, Metzger and Janssen (1928) showed a progressive decrease in hydrogen ion concentration. The hydrogen ion concentration subsequently increased when the soils were dried for a week before determinations were made. The decrease in hydrogen ions was partly attributed to ammonia and partly to reduction compounds resulting from anaerobic conditions developing in the soil.

In Ohio, Schollenberger (1928) found that when a one to one dry soil to water mixture was incubated there was a decrease in acid reaction and an increase in per cent total base saturation. With the addition of starch this effect was accentuated. A simultaneously large increase in exchangeable manganese was evidence that manganese oxides in the soil reduce and supply an active base. He found no significant change in the ammonia content of the soil and concluded that the increase in alkalinity was therefore due to reduced forms of manganese.

Robinson (1930) found that soils were made less acid by submergence for a short period except by such acidity as due to carbon

dioxide and bicarbonates. It would seem that pH would be governed by the carbon dioxide evolved.

According to Ponnamperuma (1955), Dennett (1932) conducted a field study in which he observed large differences between concentrations of hydrogen ion in the rice soil during fallow and when flooded. These he attributed not only to the formation of ammonia on waterlogging but also to a change in equilibrium between ferrous iron and ferric iron. He drew attention to the fact that ferrous iron acts as a base in submerged rice soils.

In a soil profile study Joffe (1935) contended that the anaerobic conditions prevailing in the gley horizon, which is generally waterlogged, favor reducing reactions. In the reducing process the ferric iron gives rise to ferrous iron and in the case of the hydroxide the weak base changes into the stronger ferrous base. Partly because of this fact, and that the ground waters are also enriched with bases, he concluded that one should expect a higher pH in the gley horizon.

In an investigation designed to study carbon and nitrogen transformations of waterlogged soils Screenivasan and Subrahmanyan (1935) observed that in most cases the reaction remained practically the same (pH 7.4 to 7.6) throughout the period of observation. With added energy substances the medium became acid (pH 5.7 to 5.9) within the first two weeks, after which it rose steadily to pH 7.6.

As a result of flooding a Crowley soil with distilled water, Reed and Sturgis (1939) revealed that the pH of the virgin soil increased steadily from pH 5.00 to 6.55 in a period of 18 weeks. The pH of the cultivated soil, being higher to begin with, increased under flooded condition from pH 6.45 to 7.27. In addition, the

presence of organic matter tended to raise the pH after submergence.

Mortimer (1941) submerged lake muds in a tank study with the results disclosing increases in pH, carbon dioxide, alkalinity, ammonia, ferrous and manganous compounds and a depletion of oxygen. He noted that the ammonia alone was sufficient to account for the increase in pH.

Paul and DeLong (1949) examined pH changes, after 30 days, induced by flooding a heavy textured Canadian soil with distilled water and with a 1.0 per cent glucose solution. They observed that flooding with water only tended to increase the pH slightly, whereas flooding with glucose solution produced a remarkable decrease in this characteristic. Relative to the latter they noted that in the soil-glucose solution system there was a marked "butyric" odor and considerable evolution of gas. The acids produced in that fermentation were considered responsible for the change in pH of that system.

From an investigation of wet soils Pearsall (1950) suggested that the high exchangeability of bases under reducing conditions was important in maintaining the high pH of waterlogged soils. A later study by Pearsall (1952) further indicated that the effect of changing from an oxidizing to a reducing state in wet soils also involved pH changes. The reducing condition was associated particularly with the appearance of iron and manganese in reduced forms, of lower valency and higher solubility, and also with a somewhat higher pH. His findings were further substantiated by the fact that drying and reflooding brought about reversible changes in soil pH.

Further evidence for the increase in pH of a soil on submergence was presented by Ponnamperuma (1955). He found the following tendencies:

(a) After about 34 days pH increases levelled off.

(b) An increase in organic matter content caused an increase in pH.

(c) The increase in pH was greatest for the lowest pH samples and least for the highest pH samples.

Ponnamperuma associated these tendencies with the reduction of iron and manganese.

A highly significant correlation between pH and redox potentials, in a submerged Crowley silt loam soil, was noted by Patrick (1960). At controlled soil redox potentials a decrease in potential from +500 millivolts to -100 millivolts caused an increase in pH from 4.6 to 7.0. The resulting redox potential/pH slope was 232 millivolts per pH unit. The correlation between redox potential and pH had a coefficient of -0.975.

Motomura et al. (1962) have reported paddy soils and volcanic-ash soils to increase in pH upon submergence and incubation. Upon adding rice straw or vetch the pH fell at first, rose after seven days and was fairly steady after 14 or 21 days.

Work by Takai et al. (1963) in Japan, suggested that the pH of submerged soils was greatly influenced by the amount of ferrous iron because of the close connection that existed between ferrous iron content in the soil, redox potential and pH changes.

Patrick (1964) has recently found that extractable iron in a

submerged Crowley silt loam soil responded markedly to changes in redox potential. Consequently, he explains an increase in pH accompanying a decrease in redox potential on the basis that at low redox potentials ferric hydroxide is reduced to ferrous hydroxide as follows:

$$Fe(OH)_3 + e^- \longrightarrow Fe(OH)_2 + OH^-$$

and the simultaneous production of hydroxide ions increases the pH.

Changes in Specific Conductivity

The specific conductivity of flooded soils has not been a subject of much study. Its striking characteristic is that it quickly rises even though nitrates are reduced to nitrogenous gases under these conditions. This increase in specific conductivity may nevertheless be accounted for by increases in ammonia, iron, manganese and other bases.

The earliest procedures used for determining dissolved salts in water was evaporation, between 100 and 180°C, followed by weighing. Whitney and Means (1897) proposed electrical-resistance measurements for determining the soluble salt content of soils.

Conner (1918) discovered that saturated soils had increased concentrations of several constituents such as iron, manganese, and silica.

Kitto (1938) noted that for all practical purposes the influence of dissolved free carbon dioxide on conductivity measurements may be regarded as negligible. The reason being that water rich in bicarbonate ions represses the dissociation of dissolved carbon

dioxide (CO_2) into H^+ and HCO_3^- ions, and thus the conductivity is not affected. Even in distilled water, with which the maximum effect is experienced, a saturated solution of carbon dioxide (100-150 parts per 100,000) only gave a specific conductivity with an apparent saline content of about two parts per 100,000.

Bradfield (1941) demonstrated how changes in carbon dioxide pressure quickly influenced the specific conductance of a suspension of calcium hydroxide and clay. After introducing carbon dioxide, from a cylinder, into a suspension of clay and calcium hydroxide with a pH of 8.5 the specific conductance rose from about 1.5×10^{-4} mhos/cm. to about 5.0×10^{-4} mhos/cm. in a very short lapse of time, and attained a pH of 5.37. The carbon dioxide was then turned off and the specific conductance dropped to a new and constant level of approximately 2.5×10^{-4} mhos/cm. with a pH of 7.94.

Mortimer (1941) reported that the electrical conductivity of lake mud, in an anaerobic tank experiment, rose steadily during the period of reduction. He theorized that this rise may have been partly due to the liberation of adsorbed ions as absorbing complexes were destroyed by reduction. There was a sharp fall in conductivity, after a maximum was reached, in 117 days, probably as a result of precipitation of ferrous and sulfide ions as ferrous sulfide. It was also possible that some adsorption of ions on colloidal ferrous sulfide might have taken place.

Ponnamperuma (1955) showed that there was a rapid decline in specific conductance with time in the percolates of flooded soils. The submerged soils with no drainage had five times the conductivity

of submerged soils with drainage. He suggested, therefore, that since nitrates and sulfates were then absent, the high specific conductance of the percolates from the submerged soils with no drainage was due to much higher concentrations of reduced substances than in the soils with drainage.

Changes in Redox Potential

The term oxidation-reduction potential is synonymous to "redox" potential which shall be used henceforth. When soils are submerged microbial respiration rapidly depletes the oxygen present. Conditions favorable to reduction then take place as evidenced by their reduction potentials which has been used as an index of this state. The principles involved in redox potential measurements as applied to soils are discussed by Brown (1934). Basically, the potential of the system (E_h) is proportional to the logarithm of the ratio of oxidant to reductant as well as temperature of the particular system under consideration. Also, the system must be reversible, i.e. the oxidized form readily reducible and vice versa.

Potentials are usually measured electrometrically, on a potentiometer, at a bright platinum electrode coupled to a saturated calomel electrode (S.C.E.). Since by definition, oxidation is the loss of electrons and reduction is the gain of electrons, reducing ions tend to give up electrons to the platinum electrode, which is placed in the soils, and make it more negative as they are oxidized. Oxidizing ions tend to take electrons from the electrode and make it more positive as they are reduced. When the potential is measured against a S.C.E. the potential obtained is expressed in terms of the

normal hydrogen electrode (N.H.E.) by the addition of 244 millivolts at 25°C. The value thus obtained is designated as the E_h or redox potential.

Gillespie (1920) began the pioneering work on soil redox potentials. He studied the changes in redox potentials with time when soils were flooded with and without readily decomposeable organic matter. Lower soil potentials values were closely associated with a deficiency of oxygen and increased amounts of reduced products. The rate at which they became highly reducing differed among soils. It was found that the addition of dextrose favored the development of reducing conditions.

Redox potential measurements on soils suspended in water, by Willis (1932), showed an inverse linear relation between redox potential and pH value. Evidently, liming decreased the redox potential of the fine sandy loam soil studied. The change in potential per unit change in pH dE_h/dpH, was found to be -0.060 volts. This was in good agreement with the theoretical value of -0.0591, at 25°C.

Redox potential measurements were suggested as an indicator of drainage conditions in orchard soils by Batjer (1933). For this purpose he proposed that the soil sample be shaken and allowed to stand overnight with 0.1 normal sulfuric acid before measuring its potential using two black platinum electrodes connected by means of a potassium chloride-agar bridge to a S.C.E. It appeared that good soils were normally oxidizing and that reducing conditions were an indication of an "unhealthy" state of affairs wherein the more abundant constituents of the soil, such as iron, manganese, sulfur, etc., were reduced to a lower valence form.

Heintze (1934) employed and recommended the use of the glass electrode as a satisfactory reference electrode in redox potential measurements. So closely were redox potentials dependent on the pH value that he considered that for constant pH values highly contrasted soil types would give similar redox potentials. Heintze noted a marked fall in potential after waterlogging soils in the laboratory for one or two days, and he implied that organic matter, capable of rapid decomposition, accelerated this drop in redox potential.

The effect of liming suspensions of a North Carolina peat soil was to reduce its redox potential, as found by Willis (1934). The slope of the E_h - pH curve, (dE_h/dpH), found in this study was -0.067 volts per pH unit. He concluded from this experiment that aerobic or anaerobic conditions cannot be defined by soil potentials.

Bradfield et al. (1934) according to Sturgis (1936) found that measurements of redox potentials, in suspensions of the soil in 0.1 normal sulfuric acid, promised to be a more useful index of subsoil drainage over a longer period of time than ground water observations. Working with orchard soils in New York they obtained dE_h/dpH values of -0.093 volts and -0.100 volts per pH unit for a reduced soil high in organic matter and a well oxidized soil respectively.

Work on the redox potentials of bacterial suspensions was undertaken by Yudkin (1935). He discovered that Bact. coli and Bact. alkaligenes, either alone or in the presence of succinate, showed a slow continuous fall in potential which never reached a constant value. The addition of glucose and formate, however, induced more

negative potentials, which in the case of Bact. coli soon reached a minimum value.

Burrows and Cordon (1936) added various types of organic matter to New Jersey soils in an effort to throw some light on the effect of its decomposition and attendant microbial activity on the redox potential. First they explained that the observed differences in redox potentials resulting from the addition of different kinds of organic matter may have been the result of the activity of a different microbial flora. Secondly, indications were that the type of decomposeable organic matter present in the soil was a highly important factor in the determination of the degree of prevailing reducing intensity. These workers found that the decomposition of casein resulted in positive potential levels whereas the decomposition of carbohydrates resulted in negative potentials which in turn did not differ from those produced in soil to which no organic matter was added.

The marked fall in potential, brought about by the rapid decomposition of organic matter, was reported by Darnell and Eisenmenger (1936). This fall was attributed to oxygen depletion. The effect of added ammonium sulfate and sodium nitrate on the redox potentials, of the sandy Massachusetts soil under investigation, was inconsistant. The inverse relationship between pH and E_h was verified, with the dE_h/dpH being -0.054 volts per pH unit.

Willis (1936) pointed out, from evidence of field and pot culture experiments, that redox intensities existed in arable soils but that these were not measurable by laboratory methods then in use.

It seemed improbable, except under the extreme conditions found in waterlogged or otherwise poorly aerated soils, that this technique would be useful in a direct practical sence.

The results of Sturgis (1936) show that the addition of organic matter to flooded Louisiana soils markedly increased the reduction intensity of the soil. Ferrous iron and manganous manganese accumulated in the soil as a result of submergence. The greatest intensity of reduction, from added organic matter, was more pronounced during the first three weeks following flooding. It appeared that reducing conditions developed because of the rapid removal of oxygen from the soil air or from oxides in the soil. The growth of rice was unrelated to E_h. There was not the close relationship between E_h and pH, previously reported, since the pH of the soil varied little relative to the large variations in E_h.

Stephenson *et al.* (1938), in a study of redox potentials in Oregon orchard soils, found that there was little variation in redox potential among different soil types, under field conditions, when the samples were suspended in 0.1 normal sulfuric acid prior to this determination. Likewise, different horizons showed little variation in redox potential. Insofar as organic matter was concerned, this only caused a fall in potential under waterlogged conditions. It was then concluded from this experiment that redox potential was not a dependable indication of anaerobic conditions in the soil. The dE_h/dpH for a clay loam soil studied was -0.080 volts per pH unit.

Pearsall (1938), in the course of a study of the soil complex in relation to plant communities, noted that soils containing nitrate

had potentials exceeding +350 millivolts at pH 5. It is also interesting to note that Ponnamperuma (1955) cites Aoki (1940), in Japan, as having noted a rise in potential on the addition of nitrate to a reduced soil.

Volk (1938) reported that in 132 Alabama soils various soil types had different E_h values but the differences seldom exceeded 50 millivolts. He contended that these small differences were due largely to variations in kinds and ratios of ions present rather than to the ratio of reduced to oxidized phases. Because of this he did not consider the Eh of the soil a reliable index of the state of oxidation or reduction in soils. It was concluded that variations in redox potential bore no direct relation to plant growth. It was noted that soil moisture was a very important factor in E_h. An initial increase in soil E_h, following a rain, was believed caused by the oxidation of reduced compounds in the soil through the action of oxygen dissolved in the rain-water. The further addition of moisture caused increased bacterial activity which resulted in a depletion of oxygen and consequent reduction in E_h. The average dE_h/dpH was -0.067 volts per pH unit.

Puri and Sarup (1938), working with Indian soils which had previously been leached with acid, obtained a mean value for dE_h/dpH of -0.053 volts per pH unit. The relationship between pH and Eh was so perfect that they contended that the measurement of pH should suffice for all practical purposes. These workers suggested that the universal presence of iron in all soils makes the inorganic Fe^{+3} - Fe^{+2} system the principal one for interpreting potentials therein,

although other systems can participate, ex. SO_4^{-2} - SO_3-2, MNO_2 - Mn^{++}, and NO_3^- - NO_2.

Calcareous soils contain an exceedingly active microflora and the decomposition of organic matter proceeds very rapidly. Because of this, Buehrer et al. (1939) set out to study the redox potentials of such soils with respect to organic matter decomposition, puddling, and E_h - pH relationships. Their findings were that puddling caused a marked decrease in the redox potential, particularly when the soil had been treated with 1.0 per cent alfalfa, and the dE_h/dpH was found to be -0.068 volts per pH unit.

Redox potential measurements in situ, made by Quispel (1947), in Holland, showed that it was possible to define the aerobic and anaerobic character in terms of the potential. The potentials observed in highly reduced innundated soils had the value of $E_h = \pm$ -200 to -250 millivolts. He assumed that the value of -250 millivolts was the apparent reduction potential of certain highly reducing substances in the soil under strictly anaerobic conditions. This apparent reduction potential was very unstable as slight aeration was sufficient to give rise to higher potentials. These low potentials were found under strictly anaerobic conditions. He concluded that the degree of aeration was the main factor governing the redox potential of a soil, and that the concentration of reducing substances was very important too.

Pearsall (1950) contended that by measuring the redox potential in moist soils one may get an indication of the effective oxygen concentrations. For instance, well aerated soils have potentials

of above +500 millivolts, while for waterlogged soils the potential would be below +300 millivolts, both values corrected to pH 5.0.

The results of Pierce (1953) showed a close correlation between redox potential, dissolved oxygen and pH. His figures for transects at 18 inches for a peat bog supporting spruce, which are typical, are given below.

Redox potential (m.v.)	-107	-251	-262	-213	-207	-204	-171	-185	- 90
Dissolved O_2 (ppm)	3.7	0.2	0.0	0.1	0.4	0.7	2.5	1.3	3.7
Reaction, pH	6.3	6.1	4.6	4.0	4.1	4.1	4.3	5.5	5.9

Working with controlled soil redox potentials Patrick (1960) found a very close relationship between pH and E_h. The pH increased from 4.6 to 7.0 while the E_h decreased from +500 millivolts to -100 millivolts. The E_h/pH slope obtained was -0.23 volts per pH unit.

The study of redox potentials begun by Gillespie (1920) is seen to have continued sporadically to the present date, and in fact, relatively little progress has been made. Much of the pertinent research was conducted in the early 1930's. Today the measurement of redox potential is commonly practiced in the research of flooded soils and, according to Yamane (1957), E_h values are customary used to show the degree of reduction in Japanese paddy soils.

Aomine (1962) has reviewed the literature pertinent to various aspects of redox potential of paddy soils particularly those relating it to the reduction of nitrate nitrogen to nitrogenous gases, manganic manganese to manganous manganese, ferric iron to ferrous iron and sulfate sulfur to sulfide sulfur. He noted that the redox potential

of the plowed layer (Ap horizon) of paddy soils rapidly drops to below +300 millivolts, at pH 6, after waterlogging, thereby reducing the above systems. Upon drainage, the reduced surface soils are re-oxidized and attain a potential greater than +300 millivolts. Characteristic of the B horizon of these soils is that waterlogging only affects the redox potential slightly because it remains oxidized throughout the year.

Gas Production.

Most gases from submerged soils owe their origin to anaerobic transformations. Under anaerobic conditions organic materials, as a whole, decompose much more slowly than under aerobic conditions. The anaerobic process of decomposition is characterized by the formation of various organic acids, combustible gases and other intermediate products, while under aerobic conditions, the intermediate products, if any, are quickly oxidized to carbon dioxide and water.

The notable investigations of Harrison and Aiyer, in India, began to clarify the main features of these gaseous transformations.

Harrison and Aiyer (1913) determined the composition of a large number of gas samples from rice paddy fields. They found that the gas dislodged by poking the soil in a submerged and recently transplanted rice field consisted mainly of methane, with smaller amounts of nitrogen, together with some carbon dioxide and hydrogen. Harrison and Aiyer (1915) further noted that the surface of the soil immediately in contact with the irrigation water was covered with algae and bacteria which possessed the power to oxidize methane and hydrogen to carbon dioxide and water respectively. Harrison and Aiyer (1916)

stated that a very considerable proportion of the gaseous nitrogen found in swamp paddy soils was produced through the decomposition of organic matter. Harrison (1920) observed that the proportion of hydrogen, as a constituent in paddy soil gases, varies from zero to 12 per cent, with values generally less than 3 per cent. The proportion of carbon dioxide also varied from 2 to 20 per cent, with an average of 5 per cent. He concluded that the absence of carbon dioxide and hydrogen from paddy soil gases was accounted for by bacterial reduction of carbon dioxide by hydrogen, therefore, that was why carbon dioxide and hydrogen could not persist in association in paddy soils. Aiyer (1920) identified B. fluorescens liquifaciens as the bacterium responsible for the oxidation of methane at the surface of the swamp paddy soils.

When Subramanyan (1929) added glucose to waterlogged soils he observed that at the end of 24 hours the soils developed a characteristic odor, and that they were frothy with carbon dioxide. He noted the formation of lactic, acetic, and butyric acids. In the decomposition of glucose the lactic acid was the first formed and after the third day this readily decomposed forming acetic and butyric acids.

Boruff and Buswell (1929, 1930) almost obtained the theoretical ratio of one to one for carbon dioxide to methane in the anaerobic bacterial decomposition of biological waste material. The simplest equation for cellulose decomposition they stated to be as follows:

$$C_6 H_{10} O_5 + H_2O \longrightarrow 3CO_2 + 3CH_4$$

Small amounts of hydrogen and nitrogen (3 to 5 per cent) were also produced.

The unusual appearance of carbon monoxide (CO) was reported by Robinson (1930). The observations of Harrison and Aiyer, in India, were also confirmed with respect to the disappearance of hydrogen and the formation of large quantities of nitrogen in submerged soils where blue-green algae (Chlamydomonas group) were present. Robinson pointed out that in cases where the soil is long submerged the anaerobic decomposition of proteinaceous material, in some cases, produced small quantities of hydrogen sulfide and mercaptans.

Acharya (1935a) suggested that the anaerobic decomposition of rice straw proceeded in two distinct stages. Firstly, there was the formation of organic acids such as acetic and butyric acids which were transformed from lactic acid. Secondly, there was the conversion of these acids into gaseous end-products such as methane and carbon dioxide. With respect to the factors influencing the anaerobic decomposition of rice straw Acharya (1935b) found that:

(a) 30 - 35°C was optimum.

(b) The preliminary acid formation was quite tolerant to pH changes, while gas formation was impeded above a pH of 7.5 - 8.0.

(c) The organisms responsible for anaerobic decomposition were present in the straw itself.

(d) Finely ground straw was not more quickly decomposed than unground straw.

(e) The amounts of carbon dioxide and methane produced were approximately equal.

Acharya (1935c) further demonstrated that the relative rates of

decomposition of rice straw in decreasing order were: aerobic, waterlogged, and completely anaerobic.

Sircar et al. (1940) working with rice straw confirmed the findings of Acharya in that decomposition under waterlogged conditions showed an intermediate behavior between the anaerobic process of decomposition and the aerobic process.

By using the infra-red spectrometer Arnold (1954) demonstrated that soils which were approaching saturation with moisture rapidly released large amounts of their available nitrogen as nitrous oxide. At lower moisture contents very slow evolution of this gas took place.

Using the mass spectrometer for gas analysis Najjar and Allen (1954) studied denitrification by Pseudomonas stutzeri and Bacillus subtilis, and they found that they reduced nitrite to a mixture of nitrogen gas, nitrous oxide and nitric oxide.

While studying nitrate reduction and denitrification in flooded soils, Yamane (1957), in Japan, was unable to find either methane or hydrogen after four weeks. Nitrogen evolved within one week attaining maximum evolution in two weeks time.

Alexander (1961) explained that the formation of methane in waterlogged soils resulted from the anaerobic decomposition of organic matter by a specialized physiological group of bacteria. These bacteria are strict anaerobes, differ markedly morphologically, and only metabolize short-chain, fatty acids (formic, acetic, and butyric etc.), and simple alcohols (methanol and ethanol) as organic substrates. He reiterated the findings of others in that methane production requires two or more microbial groups. One group forms organic acids and

alcohols from conventional carbohydrates and amino acids and the methane forming group of bacteria ferment the organic acids and alcohols into methane. Even though a variety of reactions lead to methane evolution under waterlogged conditions the most common is the reduction of carbon dioxide. The basic reaction may be written as follows:

$$4H_2R + CO_2 \longrightarrow 4R + CH_4 + 2H_2O$$

The substance designated as H2R is usually organic such as a fatty acid or an alcohol. It can be shown that should the carbon dioxide be labelled with isotopic carbon the methane evolved will also be labelled with the same isotopic carbon.

Methane-forming bacteria belong to the family Methanobacteriaceae.

EXPERIMENTAL

MATERIALS AND METHODS

Twenty-six Louisiana soils were used in this investigation. All soil samples were taken from the plow layer. Table 1 gives some general information on the sites from which the samples were taken. A composite sample was taken from an area approximately 20 feet in diameter. These samples were thoroughly mixed before being used. The soils were air-dried and passed through a 32-mesh sieve. The soil properties that were pertinent to this investigation are shown in Table 2.

In the nitrate, ammonia, iron, phosphorus, manganese, pH, conductivity and E_h experiments organic matter was applied as a separate treatment in the form of ground corn leaves. The rate of application was 0.25 per cent on an air-dry basis.

Particle Size Distribution Analysis.

The method of analysis was the hydrometer method proposed by Day (1956).

Prior to analysis the soil samples were prepared as follows:

Duplicate 40-gram samples were weighed out into 600 milliliter beakers. One-hundred milliliters of distilled water was added to each sample. The pH was adjusted with one normal hydrochloric acid to 3.5 to 4.0. Thirty per cent hydrogen peroxide was added to the samples placed on a hot-plate, at 60°C, to oxidize the organic matter. Any excess hydrogen peroxide was decomposed by further heating.

Table 1. General information on sites from which samples were taken.

No.	Soil	Parish	Crop	Cropping System
1	Commerce	Tensas	Cotton	Cotton with winter crop
2	Mhoon	Tensas	Soybeans	Cotton, soybeans, corn
3	Commerce	Tensas	Cotton	Cotton
4	Mhoon	Tensas	Corn	Cotton, soybeans, corn
5	Sharkey	Tensas	Soybeans	Soybeans, cotton
6	Richland (Loring)	Franklin	Cotton	Cotton
7	Olivier	Franklin	Cotton	Cotton, corn
8	Lintonia (Memphis)	Franklin	Corn	Cotton, corn
9	Gallion	Caldwell	Soybeans	Cotton, soybeans
10	Yahola	Rapides	Sugarcane	Sugarcane, cotton
11	Miller	Bossier	Cotton	Cotton, soybeans, corn
12	Yahola	Bossier	Cotton	Cotton, soybeans, corn
13	Yahola	Bossier	Cotton	Cotton, soybeans, corn
14	Sharkey	E. Baton Rouge	Sugarcane	Sugarcane, soybeans
15	Sharkey*	E. Baton Rouge	Fallow	Sugarcane
16	Sharkey*	E. Baton Rouge	Fallow	Sugarcane
17	Sharkey*	E. Baton Rouge	Fallow	Sugarcane
18	Crowley	Acadia	Sudan grass	Rice, pasture
19	Baldwin	St. Mary	Sugarcane	Sugarcane
20	Mhoon	Lafourche	Sugarcane	Sugarcane
21	Baldwin	St. Mary	Sugarcane	Sugarcane
22	Baldwin	St. Mary	Sugarcane	Sugarcane
23	Midland	Acadia	Rice	Rice, pasture
24	Richland (Loring)	Lafayette	Sugarcane	Sugarcane, soybeans
25	Commerce	W. Baton Rouge	Sugarcane	Sugarcane, soybeans
26	Iberia	St. Mary	Sugarcane	Sugarcane

*Formerly classified as Mhoon

Table 2. Some chemical and physical properties of the soils investigated.

No.	Name	Sand %	Silt %	Clay %	Texture	Particle Density
1	Commerce	43.5	42.5	14.0	Loam	2.65
2	Mhoon	4.9	51.7	43.4	Silty clay	2.65
3	Commerce	43.9	40.8	15.3	Loam	2.64
4	Mhoon	9.8	53.3	36.9	Silty clay loam	2.65
5	Sharkey	1.9	22.7	75.4	Clay	2.61
6	Richland	2.6	78.3	19.1	Silt loam	2.62
7	Olivier	3.9	75.7	20.4	Silt loam	2.64
8	Lintonia	7.7	66.7	25.6	Silt loam	2.67
9	Gallion	20.3	68.3	11.4	Silt loam	2.60
10	Yahola	32.6	49.6	17.8	Silt loam	2.64
11	Miller	6.3	47.2	46.5	Silty clay	2.61
12	Yahola	61.8	26.8	11.4	Sandy loam	2.64
13	Yahola	26.7	47.0	26.3	Loam	2.64
14	Sharkey	25.0	39.4	35.6	Clay loam	2.67
15	Sharkey	74.7	13.8	11.5	Sandy loam	2.65
16	Sharkey	2.8	56.0	41.2	Silty clay	2.65
17	Sharkey	41.2	48.3	10.5	Loam	2.65
18	Crowley	10.2	73.1	16.7	Silt loam	2.64
19	Baldwin	12.6	58.7	28.7	Silty clay loam	2.66
20	Mhoon	3.5	62.0	34.5	Silty clay loam	2.68
21	Baldwin	12.8	51.4	35.8	Silty clay loam	2.62
22	Baldwin	2.5	63.1	34.4	Silty clay loam	2.63
23	Midland	3.4	58.6	38.0	Silty clay loam	2.64
24	Richland	1.8	82.7	15.5	Silt loam	2.59
25	Commerce	52.7	38.3	9.0	Sandy loam	2.64
26	Iberia	0.4	25.9	73.7	Clay	2.71

[1]Determined immediately after flooding

After cooling the samples from the hot plate they were transferred into centrifuge tubes. The centrifuge was run at 1500 revolutions per minute for five minutes. At the end of the centrifuging period the supernatant was decanted and discarded. The soil was further washed with 95 per cent ethyl alcohol until found free of chlorides as tested by adding a few drops of 0.1 normal silver nitrate.

One of the chloride-free samples was transferred into a tared beaker and dried in an oven at 105°C until a constant weight was obtained. The other chloride-free sample was transferred into a 600 milliliter beaker and 50 milliliters of dispersing agent (10 per cent Calgon) was added. After diluting to approximately 300 milliliters with distilled water the sample was quantitatively transferred to a dispersing cup and mixed for five minutes with a motor mixer. Finally, this was transferred to a 1000 milliliter graduated cyclinder and brought to volume with distilled water.

The textural names of the soils were determined on the basis of the particle size distribution analysis using the scheme proposed in Soil Survey Manual, Handbook No. 18, U.S.D.A.

Particle Density

Approximately 100-150 grams of soil were transferred into a clean, tared 250 milliliter volumetric flask. The flask was placed in an oven at 105°C and dried until a constant weight was attained. Sufficient distilled water was added to bring the total volume of soil plus water to about 200 milliliters. The flask was subsequently placed in an oven at 105°C until the soil temperature reached

90-100°C. The flask was removed, allowed to cool just long enough so that it could be handled, and attached to a vacuum line. By reducing the pressure in the flask the air could be boiled out of the saturated soil. After boiling for five to ten minutes under this reduced pressure the flask was stoppered and allowed to cool to room temperature. Finally, the flask was filled to mark with distilled water, weighed, and particle density calculated.

Particle density was calculated in order to calculate the volume of soil in connection with the gas production and denitrification experiments.

Organic Matter

The dry combustion method was the method used for total organic carbon content. Approximately two-gram soil samples were ignited in an electric combustion furnace at 950°C for ten minutes in an adjusted flow of oxygen. The carbon dioxide produced in the combustion of the organic matter was absorbed in a tube filled with layers of glass wool and Ascarite, and weighed gravimetrically. The organic matter was estimated from the organic carbon by multiplying by the factor 1.724, (Van Bemmelen factor). This factor comes from the assumption that the organic matter of the average soil contains 58 per cent carbon.

One-Third Atmosphere Moisture Percentage

The one-third atmosphere moisture percentage was determined by using the porous plate apparatus as proposed by Richards (1948).

The moisture retained (dry weight basis) by the soil brought

to hydraulic equilibrium with a permeable membrane at a soil moisture tension of one-third atmosphere was determined. This one-third atmosphere moisture value closely approximates the moisture equivalent or field capacity of most soils and was used in connection with a nitrate reduction experiment.

Nitrate Reduction

Two experiments were undertaken to measure nitrate reduction rates under slightly different conditions. The first experiment (Experiment I) was designed to quantitatively measure the rate of nitrate nitrogen loss from the soils as a result of flooding a moist soil with and without additional organic matter. The second nitrate reduction experiment (Experiment II) was designed to qualitatively estimate the rate of nitrate nitrogen loss from soils as a result of adding a nitrate salt to previously flooded highly reduced soils, with and without organic matter having previously been added.

Experiment I: Eighteen five-gram air-dry soil samples of each soil studied were weighed into 15 x 125 millimeter test tubes and then wetted with distilled water to one-third atmosphere moisture values. The samples were incubated for two weeks at 30°C. Nitrate nitrogen was then added at the rate of 0.125 milligrams per five grams of air-dry soil or approximately 250 parts per million. This was added by dissolving potassium nitrate in distilled water and flooding the sample with two milliliters of this solution using a Filamatic vial filler. It was found necessary after the addition

of the nitrate solution to place the tubes under vacuum in a desiccator to drive out any air, thereby wetting the entire soil mass. The submerged soils were sampled at 18 different times during a 32-day incubation period. After sampling they were stored in a freezer maintained at -20°C, until the experiment terminated, at which time all of the samples were analyzed for nitrate nitrogen.

Each test tube containing the frozen sample was wrapped in aluminum foil, cracked in a vice and transferred quanitatively to a 125 millliliter Erlenmeyer flask. The nitrate ions in the samples were extracted by shaking for 30 minutes on a mechanical shaker with 30 milliliters of distilled water in the presence of a small amount of calcium hydroxide. Aliquots of this filtrate were quantitatively analyzed for nitrate using the phenoldisulfonic acid test.

Experiment II. One hundred-gram samples of each of the soils were flooded in 35 x 200 millimeter test tubes with an equal volume of water. A layer of clear mineral oil, approximately 0.5 centimeters thick, was then floated on the surface in order to keep oxygen from diffusing into the surface water. After 37 days of submergence nitrate nitrogen was added to each of the samples at the rate of five milligrams per 100 grams of air-dry soil or approximately 50 parts per million. This was added in the form of potassium nitrate dissolved in five milliliters of distilled water. The samples were maintained at a room temperature of approximately 25°C.

The samples for nitrate analysis were taken by introducing a glass tube into the soil and withdrawing some of the soil-water

suspension. The samples were centrifuged in test tubes with a pinch of calcium hydroxide. The supernatant liquid was qualitatively analyzed for nitrate nitrogen by a modification of the phenol-disulfuric acid method. In this method two drops of the supernatant liquid on a clean porcelain spot plate were evaporated to dryness in a draft oven. A drop of phenoldilsulfonic acid was added and mixed with the dried extract, followed by a drop of water. Ammonium hydroxide (1/1) was employed to shift the pH to the alkaline range where the presence of nitrate produced a yellow color. This test was able to detect nitrates at concentrations as low as one to two parts per million. When two consecutive sampling days showed a negative nitrate reaction the reduction of nitrates was considered complete and further sampling was ceased. The rate of nitrate reduction was estimated by dividing the original nitrate concentration by the number of days required to reduce the nitrate.

Ammonia Accumulation

The production of ammonium nitrate under flooded conditions was studied by flooding duplicate five-gram samples of air-dry soil in 15 x 125 millimeter test tubes with five milliliters of distilled water. The samples were incubated for 30 days at 30°C. at which time they were sampled and kept frozen at -20°C until analyzed.

Each test tube containing the frozen sample was wrapped in aluminum foil, cracked in a vice and transferred quantitatively to a 125 milliliter Erlenmeyer flask. The ammonium ions in the samples were extracted by shaking for 30 minutes on a mechanical shaker

with 30 milliliters of 10 per cent sodium chloride solution of pH 2.5. Aliquots of this filtrate were quantitatively analyzed for ammonium nitrogen by the direct nesslerization method recommended by The American Public Health Association Inc., (1946).

Iron Reduction

Changes in ferric and ferrous iron caused by submergence were studied in an experiment similar to that used for Ammonia Accumulation. The samples were incubated for 30 days at 30°C.

Ferric and ferrous iron were extracted by shaking for 20 minutes on a mechanical shaker with 50 milliliter of one normal sodium acetate solution of pH 2.8. The iron extracted was determined by the colorimetric α, α dipyridyl method according to the procedure of Kumada and Asami (1958). Although this reaction only involves ferrous iron, ferric iron could be determined by first reducing the ferric iron to the ferrous iron with 5 per cent hydroxylamine hydrochloride and then analyzing for total iron and subtracting the ferrous iron content.

Extractable Phosphorus:

Extractable phosphorus changes in flooded soils were studied in an experiment set up similar to those previously described for Ammonia Accumulation and Iron Reduction. The samples were incubated for 30 days at 30°C.

The phosphorus in the samples was extracted by shaking for 15 minutes on a mechanical shaker with 100 milliliters of 0.1 normal hydrochloric acid and 0.03 normal ammonium fluoride solution. Aliquots of this filtrate were colorimetrically analyzed for phosphorus by

the intensity of color of the molybdate blue complex formed by the reaction of orthophosphate with ammonium molybdate in the presence of the reducing agent stannous chloride. The analysis of phosphorus was based on the method of Dickman and Bray (1940).

Manganese Reduction

The filtrate obtained in the above Iron Reduction experiment was used to analyze for manganese as well.

Manganese was determined by a modification of the method developed by Peech et al. (1947). A five-milliliter aliquot was pipetted into a 50 milliliter beaker and this was evaporated to dryness in a steam bath. Ten milliliters of concentrated nitric acid was added to oxidize the organic matter and volatilize the chlorides as hydrogen chloride. The residue was treated with 35 milliliters of distilled water and five milliliters of 85 per cent phosphoric acid in order for the latter to form a colorless complex with ferric iron. The manganese was ultimately oxidized with 0.3 gram of sodium periodate to the colored permanganate ion. The cooled solution was transferred to a 50 milliliter volumetric flask, made to volume and read on a Fisher electrophotometer.

Changes in pH.

Fifty grams of air-dry soil were flooded with 50 milliliters water in a 150 milliliter beaker. The samples were kept at a room temperature of approximately 25°C. pH measurements were made at the start (30 minutes after flooding) and at monthly intervals for four months.

These determinations were made with a Beckman Zeromatic pH meter with glass-calomel electrodes which had been standardized at pH values of 7.0 and 5.0.

Changes in Specific Conductivity.

Seventy-five grams of air-dry soil were flooded with 75 milliliters distilled water in a 250 milliliter Erlenmeyer flask. The samples were kept at a room temperature of approximately 25°C. Specific conductivity measurements were made at the start (30 minutes after flooding) and after one month. Specific conductivity was determined in a standard Bureau of Soils soil resistance cup with a Conductance Bridge containing a cathode ray tube (electronic eye) as the null indicator. The cell constant of the conductance cell was first determined by measuring the electrical resistance of a 0.01 molar potassium chloride solution. The specific conductance, in millinhos per centimeter, was equal to the cell constant divided by the measured electrical resistance in millimhos. Reference is made to Jackson (1958).

Changes in Redox Potential.

This experiment was designed to measure the redox potential at different times after flooding. Special platinum electrode tubes were constructed by sealing a piece of 18-guage platinum wire at the side of a 20 x 150 millimeter Pyrex test tube as shown in Figure 1. Before starting the experiment the platinum electrodes were cleaned electrolytically for three minutes in one normal hydrochloric acid. This was done by connecting the positive and negative poles of a

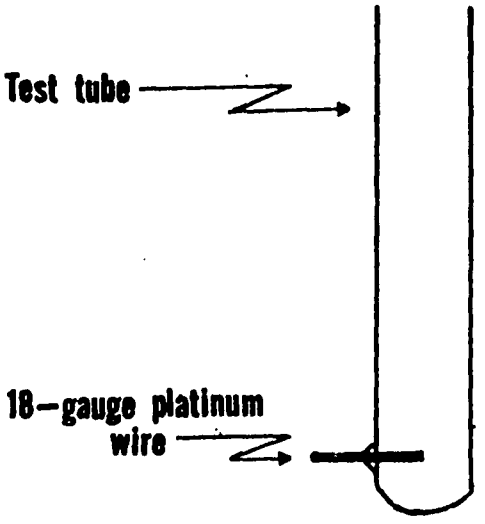
22 1/2 volt dry cell battery to a carbon electrode and the platinum electrode respectively. In addition, the platinum electrodes were checked by comparing the E_h of quinhydrone solutions in pH 4.00 and 7.00 buffer solutions at 25°C, with previously calculated values appearing in the Beckman Instruments Bulletin 99-D.

Fifteen grams of air-dry soil were weighed out in these electrode tubes and flooded with an excess of distilled water. These samples were then incubated at 30°C. E_h measurements were made within minutes after flooding, 12 hours after flooding and subsequently at daily intervals for 32 days.

Redox potential measurements were made with a Beckman Zeromatic pH meter by means of the platinum electrode and a saturated calomel half cell. Redox potential values were converted into millivolts versus the normal hydrogen electrode by the addition of 244 millivolts at 25°C.

Carbon Dioxide and Methane Production.

This experiment was designed to identify and measure the gases evolved when soils are flooded for an extended period. Special glass incubation jars were constructed as illustrated in Figure 2. The volumes of 26 such incubation jars were accurately determined by filling the enclosed parts with distilled water of known temperature and weighing. Equal weights of air-dry soil samples of each soil and distilled water were then weighed into respective jars so that the volume of soil plus distilled water occupied one-half of the total volume of the incubation jar. These calculations were made individually for each soil considering soil particle density, per cent air-dry



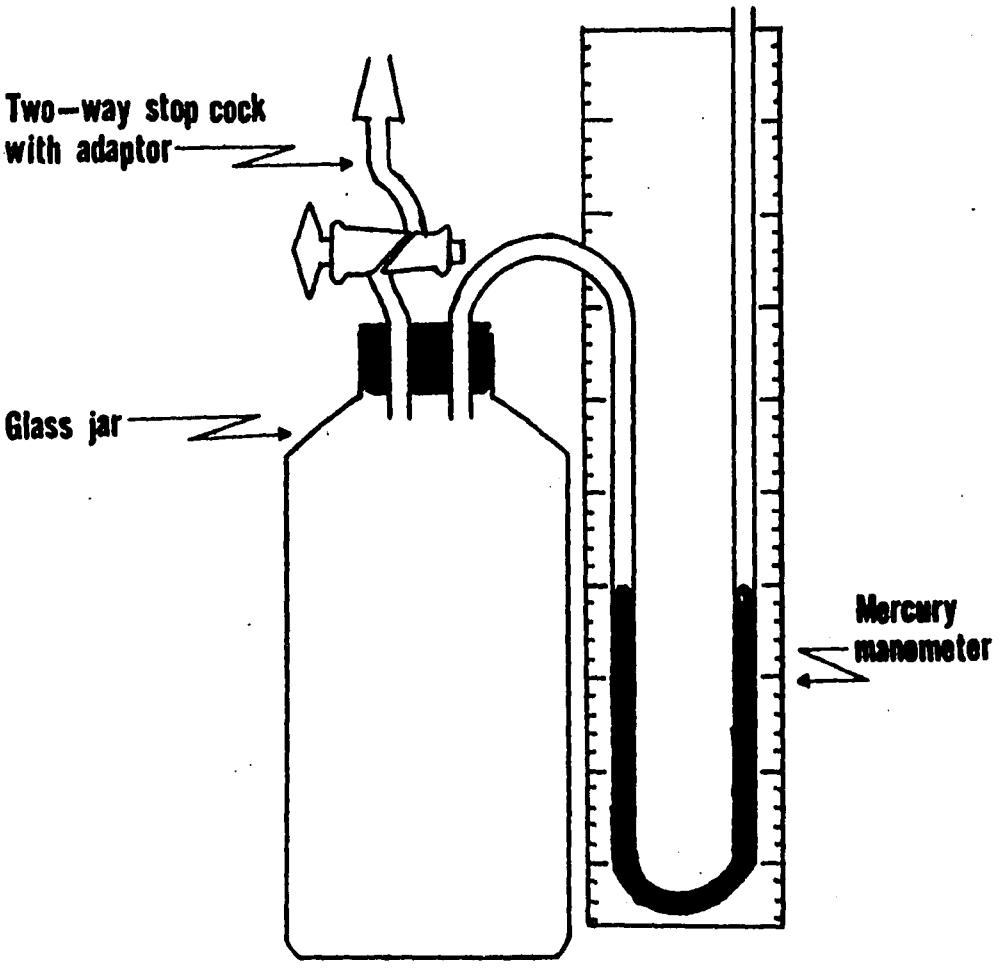


Figure 1. Platinum electrode tube used for E_h measurement in submerged soil samples.

Figure 2. Glass incubation jar used for gas evolution and denitrification measurements.

moisture of soil, and density of the distilled water at a given temperature. The flasks were stoppered with a number eight rubber stopper containing a mercury manometer side arm and a high vacuum two-way stop cock with an adaptor. These flooded soils were incubated at 30°C.

Pressure readings were taken four and one-half months later just prior to gas analysis. At sampling the adaptor was directly attached to a Consolidated Electrodynamic mass spectrometer (Type 21-611) and a small portion of the gaseous phase introduced by carefully manipulating the two-way stop cock. The mass spectrometer recorded peaks of mass/charge (m/e) ratios on chart paper. The peak heights measured for determining methane and carbon dioxide were m/e 15 and 22 respectively. The total volume of gas was calculated at standard temperature and pressure considering the manometer pressure, atmospheric pressure, volumes of container, and incubation temperature. The volume of carbon dioxide and methane were then calculated from this data and the mass spectrometer data. Gases of known composition were used to calibrate the mass spectrometer.

Denitrification.

Upon completing the gas production experiment, the incubation jars were placed under vacuum for several days to extract all gases from the soil. The jars were then purged by alternately evacuating and flushing with helium. Finally nitrate nitrogen, as potassium nitrate, was added at the rate of 46.25 milligrams per sample or approximately 250 parts per million. Sucrose was also added as an energy source at the rate of 925 milligrams per sample or approximately

0.5 per cent. Both the nitrogen and the energy source were added by pipetting five milliliters of a solution containing dissolved potassium nitrate and sucrose at the concentrations of 66.76 grams and 185 grams per liter respectively. The flooded soils were placed under anaerobic conditions by alternately applying a vacuum and flushing with the inert gas argon. The attainment of extremely low oxygen and nitrogen concentrations within the incubation jars was confirmed by analyzing a gas sample with the mass spectrometer. The jars were incubated at 30°C under an argon atmosphere approximately equal to atmospheric pressure.

Pressure readings were taken after eight, nine and ten days just prior to sampling and analysis. The incubation jars were sampled and the gases analyzed with the mass spectrometer as described for the Carbon Dioxide and Methane Production experiment. There was never any evidence of nitrous oxide appearing at peak m/e 30. The peak height measured for calculating nitrogen was m/e 28. This was corrected for the background of the instrument and the contribution of carbon dioxide to the magnitude of m/e 28. The volume of nitrogen at standard temperature and pressure was calculated from manometer pressure, atmospheric pressure, volume of container, incubation temperature and mass spectrometer readings. The mass spectrometer was calibrated using gases of known mixture.

Finally, a spot test for nitrate nitrogen in the soil was conducted as previously described for the qualitative analysis of nitrate under Nitrate Reduction, Experiment II.

RESULTS AND DISCUSSION

Table 3 presents the nitrate reduction rates obtained by the quantitative methods described in Materials and Methods. The quantitative rates were determined statistically by calculating the regression coefficient of the linear regression equation by the method of least squares. The qualitative rates were determined by dividing the parts per million of nitrate nitrogen added by the number of days required for the test to indicate the absence of nitrates.

Table 4 shows the results of the denitrification experiment.

The results of other biological, physicochemical and chemical analyses are presented in Tables 5 to 12.

The correlation coefficients (r) for physical, biological, physicochemical and chemical properties of the treatments not receiving additional organic matter are presented in Tables 13 to 15. The correlation coefficients for these properties of the treatments which received additional organic matter are not presented since similar correlations existed.

Nitrate Reduction

Experiment I: Table 3 shows that all the soils had the capacity to reduce nitrates under submergence. The nitrate reduction rates ranged from 0.49 parts per million per day in the Commerce sandy loam (soil #25) to 9.42 parts per million per day in the Iberia clay (soil #26).

Table 3. Nitrate reduction rates under submerged condition with and without added organic matter (0.25% ground corn leaves).

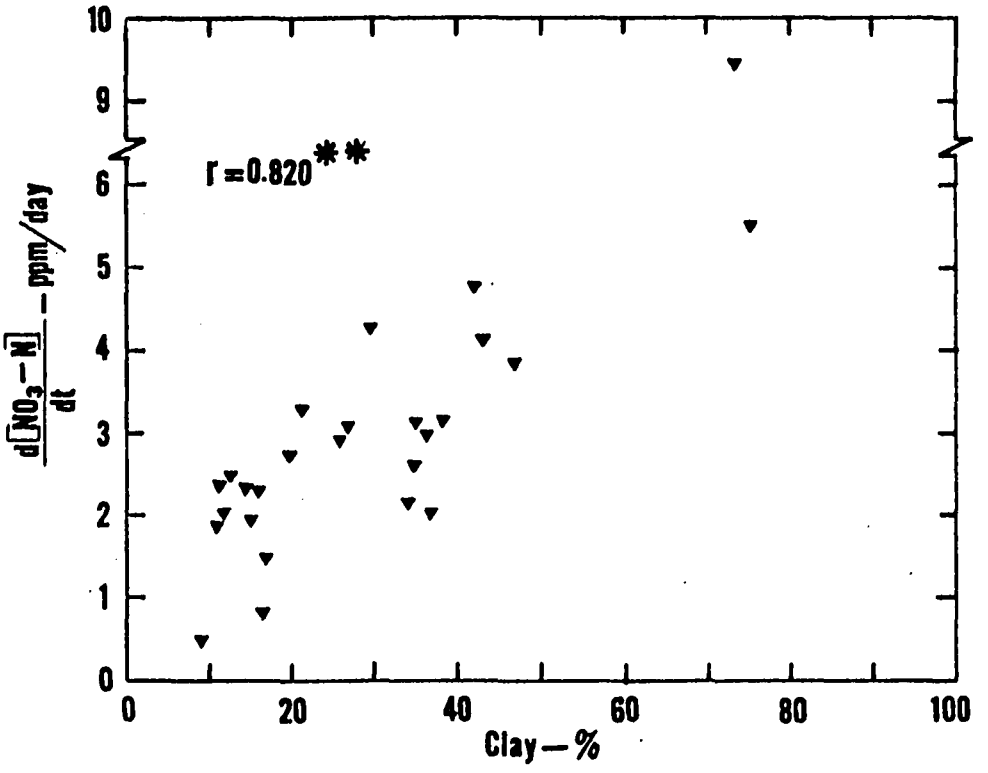
No.	Soil		Quantitative Nitrate Reduction (ppm/day) Flooded with No O.M. added	Flooded with O.M. added	Difference	Qualitative Nitrate Reduction (ppm/day)[1] Flooded with No O.M. added	Flooded with O.M. added	Difference
1	Commerce	l	2.31	2.67	+0.36	2.44	3.84	+1.40
2	Mhoon	sic	4.08	5.17	+1.09	3.89	5.08	+1.19
3	Commerce	l	1.94	3.51	+1.57	2.33	2.69	+0.36
4	Mhoon	sicl	2.06	6.57	+4.51	3.36	3.92	+0.56
5	Sharkey	c	5.49	7.84	+2.35	4.27	4.78	+0.51
6	Richland	sil	2.67	5.90	+3.23	1.62	2.42	+0.80
7	Olivier	sil	3.35	6.42	+3.07	1.79	2.45	+0.66
8	Lintonia	sil	2.93	5.75	+2.82	1.06	2.46	+1.40
9	Gallion	sil	2.46	3.28	+0.82	4.42	4.44	+0.02
10	Yahola	sil	1.56	3.29	+1.73	1.08	2.27	+1.19
11	Miller	sic	3.87	4.15	+0.28	2.01	3.89	+1.88
12	Yahola	sl	1.94	2.64	+0.70	1.41	4.13	+2.72
13	Yahola	l	3.10	5.90	+2.80	2.48	3.22	+0.74
14	Sharkey	cl	2.20	3.13	+0.93	1.44	2.92	+1.48
15	Sharkey	sl	2.05	3.07	+1.02	1.44	6.73	+5.29
16	Sharkey	sic	4.71	4.80	+0.09	3.73	3.74	+0.01
17	Sharkey	l	2.44	3.67	+1.23	2.35	2.86	+0.51
18	Crowley	sil	0.84	1.81	+0.97	1.85	2.34	+0.49
19	Baldwin	sicl	4.34	6.32	+1.98	2.30	2.92	+0.62
20	Mhoon	sicl	3.11	3.04	-0.07	4.42	4.73	+0.31
21	Baldwin	sicl	3.02	5.90	+2.88	2.55	2.96	+0.41
22	Baldwin	sicl	2.59	4.47	+1.88	4.08	4.78	+0.70
23	Midland	sicl	3.10	4.67	+1.57	2.37	2.49	+0.12
24	Richland	sil	2.24	1.91	-0.33	1.63	3.16	+1.53
25	Commerce	sl	0.49	0.87	+0.38	3.14	5.97	+2.83
26	Iberia	c	9.42	9.64	+0.22	4.58	4.57	-0.01

[1]The quantitative and qualitative rates were determined under different conditions.

The quantitative nitrate reduction rates were positively highly significantly related to clay, organic matter, carbon dioxide production and methane production with correlation coefficients of 0.820, 0.596, 0.719 and 0.722 respectively, Table 14. Apparently clayey soils which have large amounts of organic matter either have a larger and/or more variable denitrifying population than the less clayey soils, or the greater energy source results in a higher rate of denitrification. The relationships between nitrate reduction and clay and between nitrate reduction and organic matter are shown in Figures 3 and 4. The oxidation of soil organic matter liberates the energy required for the reduction of nitrate nitrogen. The close association between per cent clay and per cent organic matter ($r = 0.849$) is shown in Figure 5. It is likely that the apparent relationship of nitrate reduction rate to clay content was really an indirect relationship that was due to the close association of nitrate reduction with organic matter and the close relationship of organic matter to clay.

The fact that nitrate reduction is a biological process is manifested by its close correlation with both carbon dioxide production and methane production. These gases are considered the anaerobic end products of bacterial decomposition of carbonaceous materials.

The addition of 0.25 per cent ground corn leaves almost invariably increased the nitrate reduction rates. The nitrate reduction rates varied from 0.87 parts per million per day in the Commerce sandy loam (soil #25) to 9.64 parts per million per day in the Iberia clay (soil #26), Table 3. The increase in nitrate reduction rate as a result of the addition of organic matter was by no means consistent,



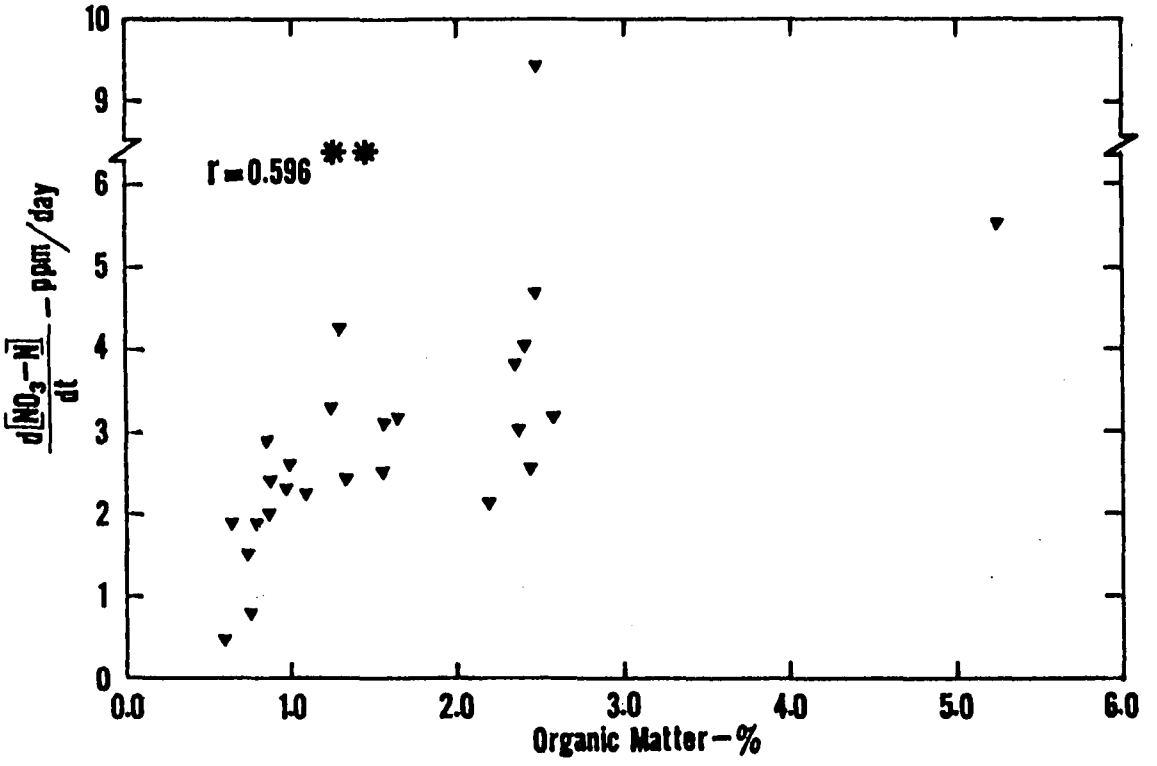


Figure 3. Correlation between nitrate reduction rate and clay content.

Figure 4. Correlation between nitrate reduction rate and organic matter content.

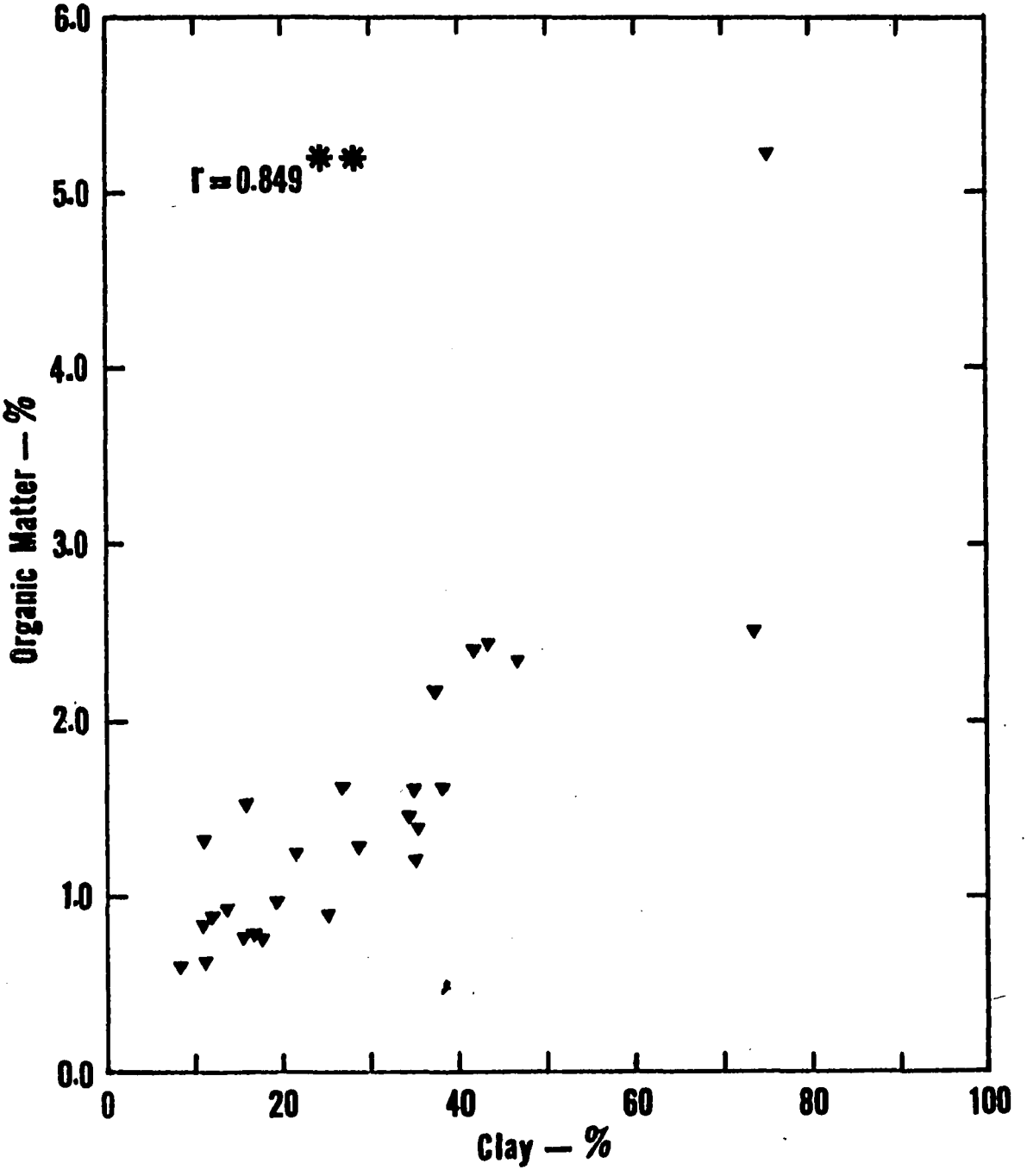


Figure 5. Correlation between soil organic matter content and soil clay content.

thereby showing that each soil responded differently to added organic matter. The extent to which these soils reacted to additional energy source was probably determined more by the inherent denitrifying population than by either the amounts of clay and organic matter initially in the soils. For example, the Mhoon silty clay loam (soil #4) exhibited an increase in nitrate reduction of 4.51 parts per million per day while the Mhoon silty clay loam (soil #20) exhibited a decrease in nitrate reduction rate of 0.07 parts per million per day. These soils had comparable amounts of clay and organic matters.

The fact that nitrate reduction was also correlated with the ammonia content after 30 days of submergence is not because this ammonia was a product of nitrate reduction but rather that this ammonia came from the mineralization of part of the organic nitrogen. Since organic matter was in turn correlated with nitrate reduction it was not surprising to find that ammonia was correlated with nitrate reduction. Similarly, the correlations of nitrate reduction with ferrous iron and specific conductivity are probably indirect due to their correlations with clay and organic matter. No logical explanation can be offered for the negative relationship with pH. In general, high pH values favor denitrification as found by Nommik (1956) and Bremner and Shaw (1958).

Experiment II: The nitrate reduction rates as determined qualitatively are also shown in Table 3. These results also show that nitrate reduction is a phenomenon exhibited by all the soils under submergence. In this experiment the nitrate reduction rates for soils flooded without additional organic matter varied from 1.06 parts per

million per day for the Lintonia silt loam (soil #8) to 4.58 parts per million per day for the Iberia clay (soil #26). The fact that these rates differ somewhat from the rates obtained by the quantitative method in Experiment I can probably be attributed to the different conditions under which the experiment was conducted. The nitrate reduction rates determined by this method were also found to be positively highly significantly correlated with clay, organic matter, carbon dioxide production and methane production with r values of 0.546, 0.627, 0.688, and 0.717, respectively, as shown in Table 14. Comparing these r values with the corresponding r values obtained in Experiment I indicate that approximately similar correlations were obtained in this qualitative method.

Soils receiving 0.25 per cent ground corn leaves reduced nitrates at rates ranging from 2.27 parts per million per day for the Yahola silt loam (soil #10) to 6.73 parts per million per day in the Sharkey silt loam (soil #15). The nitrate reduction rates were almost invariably higher than without added organic matter although the addition of organic matter did not increase nitrate reduction to the same extent in every soil. The addition of organic matter did not favor nitrate reduction in any group of soils, such as those that were originally either high or low in clay or either high or low in organic matter. The correlations of nitrate reduction with ammonia production, ferrous iron, and specific conductivity are similar to the correlations obtained for Experiment I. No logical explanation can be given to the correlation with phosphorus except that possibly in the decomposition of organic matter phosphorus mineralization occurred.

Denitrification

An examination of Table 4 shows that nitrate added to highly reduced soils was reduced to nitrogen gas to varying degrees ranging from 0.3 per cent of the total added as nitrate after eight days in the Commerce loam (soil #3) to 80.0 per cent after ten days in the Yahola loam (soil #13).

Since the study was conducted under anaerobic and otherwise identical conditions, the differences were due to the individual capacity for each soil to reduce nitrate nitrogen to nitrogen gas. The denitrifying organisms developing with the added available energy supply used the combined oxygen in the nitrate form as a hydrogen acceptor.

The mass spectrometer analysis did not detect appreciable quantities of the other gaseous products of denitrification such as nitrous oxide and nitric oxide. This suggests that these intermediate products must have been transitory in nature or the time of sampling missed the reduction stage in which these were present, obviously in small amounts. Nitrate nitrogen was absent immediately after gas analysis as determined by the qualitative phenoldisulfonic acid spot test described in Materials and Methods. This would indicate that the nitrate nitrogen added was then present in other intermediate products such as nitrite. It is also possible that some of the nitrate was assimilated as a nutrient by microorganisms.

Ammonia Accumulation.

The results shown in Table 5 clearly indicate that flooding

Table 4. Nitrogen evolved as a result of denitrification of added nitrate nitrogen to waterlogged soils.

No.	Soil		Days from addition to analysis	N_2 - c.c. at S.T.P.	N_2 evolved as % of Total added
1	Commerce	1	8	8.3	22.5
2	Mhoon	sic	8	3.2	8.7
3	Commerce	1	8	0.1	0.3
4	Mhoon	sicl	8	10.2	27.7
5	Sharkey	c	8	4.1	11.0
6	Richland	sil	8	1.1	2.9
7	Olivier	sil	8	4.0	10.7
8	Lintonia	sil	8	10.4	28.2
9	Gallion	sil	8	11.6	31.4
10	Yahola	sil	8	10.9	29.6
11	Miller	sic	8	21.4	57.9
12	Yahola	sil	8	6.8	18.4
13	Yahola	1	10	29.6	80.0
14	Sharkey	cl	10	10.0	26.4
16	Sharkey	sic	10	15.9	42.9
17	Sharkey	1	10	13.9	37.7
18	Crowley	sil	10	14.9	40.4
19	Baldwin	sicl	9	24.4	65.9
20	Mhoon	sicl	9	10.6	28.6
21	Baldwin	sicl	9	14.1	38.0
22	Baldwin	sicl	9	13.2	35.6
23	Midland	sicl	9	15.2	41.2
24	Richland	sil	9	14.2	38.5
25	Commerce	sl	9	22.3	60.4
26	Iberia	c	9	16.7	45.0

Sample No. 15 was not analyzed because excessive gas production blew the mercury out of the manometer.

Table 5. Ammonia production under submerged condition for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		Parts per million of ammonium nitrogens					
			Initial	Flooded with No O.M. added	Flooded with O.M. added	Resulting from flooding	Resulting from flooding with O.M.	Difference due to O.M.
1	Commerce	l	8.5	44.7	122.2	+ 37.2	+113.7	+ 76.5
2	Mhoon	sic	12.0	101.7	191.8	+ 89.7	+179.8	+ 90.1
3	Commerce	l	22.2	44.6	143.2	+ 22.4	+121.0	+ 98.6
4	Mhoon	sicl	7.3	72.2	133.2	+ 64.9	+125.9	+ 61.0
5	Sharkey	c	16.7	140.6	142.4	+123.9	+125.7	+ 1.8
6	Richland	sil	13.6	66.4	204.8	+ 52.8	+191.2	+138.4
7	Olivier	sil	13.4	65.3	209.4	+ 52.5	+196.0	+143.5
8	Lintonia	sil	13.7	52.9	135.6	+ 39.2	+121.9	+ 82.7
9	Gallion	sil	11.0	70.9	125.9	+ 59.9	+114.9	+ 55.0
10	Yahola	sil	4.8	36.2	95.4	+ 31.4	+ 90.6	+ 59.2
11	Miller	sic	9.4	49.3	128.6	+ 39.9	+119.2	+ 79.3
12	Yahola	sl	7.4	16.3	45.1	+ 8.9	+ 37.7	+ 28.8
13	Yahola	l	3.9	34.6	99.0	+ 30.7	+ 95.1	+ 64.4
14	Sharkey	cl	5.3	24.0	83.3	+ 18.7	+ 78.0	+ 59.3
15	Sharkey	sl	3.6	19.4	78.5	+ 15.8	+ 74.9	+ 59.1
16	Sharkey	sic	12.8	72.5	156.8	+ 59.7	+144.0	+ 84.3
17	Sharkey	l	7.2	40.4	132.4	+ 33.2	+125.2	+ 92.0
18	Crowley	sil	13.9	50.0	133.8	+ 36.1	+119.9	+ 83.8
19	Baldwin	sicl	44.2	80.9	244.3	+ 36.7	+200.1	+163.4
20	Mhoon	sicl	8.7	105.9	136.6	+ 97.2	+127.9	+ 30.7
21	Baldwin	sicl	22.3	92.0	231.8	+ 69.7	+209.5	+139.8
22	Baldwin	sicl	40.3	134.4	171.2	+ 94.1	+130.9	+ 36.8
23	Midland	sicl	10.2	100.4	149.6	+ 90.2	+139.4	+ 49.2
24	Richland	sil	14.9	44.1	135.4	+ 29.2	+120.5	+ 91.3
25	Commerce	sl	15.8	34.3	93.4	+ 18.5	+ 77.6	+ 59.1
26	Iberia	c	67.7	109.1	250.7	+ 41.4	+183.0	+141.6

brought about tremendous increases in ammonium nitrogen ranging from a concentration of 16.3 parts per million in the Yahola sandy loam (soil #12) to a concentration of 140.6 parts per million in the Sharkey clay (soil #5). From Table 14 it may be seen that the ammonia concentration after 30 days submergence was highly correlated with per cent organic matter originally in the soil with an r value of 0.776. This relationship is shown in Figure 6. This shows that soils rich in organic matter release large amounts of ammonia. Under submerged conditions organic matter was decomposed and the mineralization of organic nitrogen stopped at the ammonia stage because further oxidation of ammonia was inhibited by the anaerobic conditions. The amount of nitrogen available to a rice crop is obviously dependent on the organic matter content of the soil.

With the addition of 0.25 per cent ground corn leaves flooding caused an even greater release of ammonia ranging from a concentration of 45.1 parts per million in the Yahola sandy loam (soil #12) to 250.7 parts per million in the Iberia clay (soil #26), Table 5. Even though the addition of organic matter resulted in larger concentrations of ammonia such increases were not constant. The increases of ammonia due to the addition of corn leaves ranged from 1.8 parts per million in the Sharkey clay (soil #5) to 163.4 parts per million in the Baldwin silty clay loam (soil #19). Since the amount of nitrogen added as corn leaves was approximately 75 parts per million (0.25 per cent corn leaves added containing 3.0 per cent nitrogen) it is obvious that the added organic matter stimulated the mineralization of nitrogen in excess of that contained in the corn leaves in some of the soils.

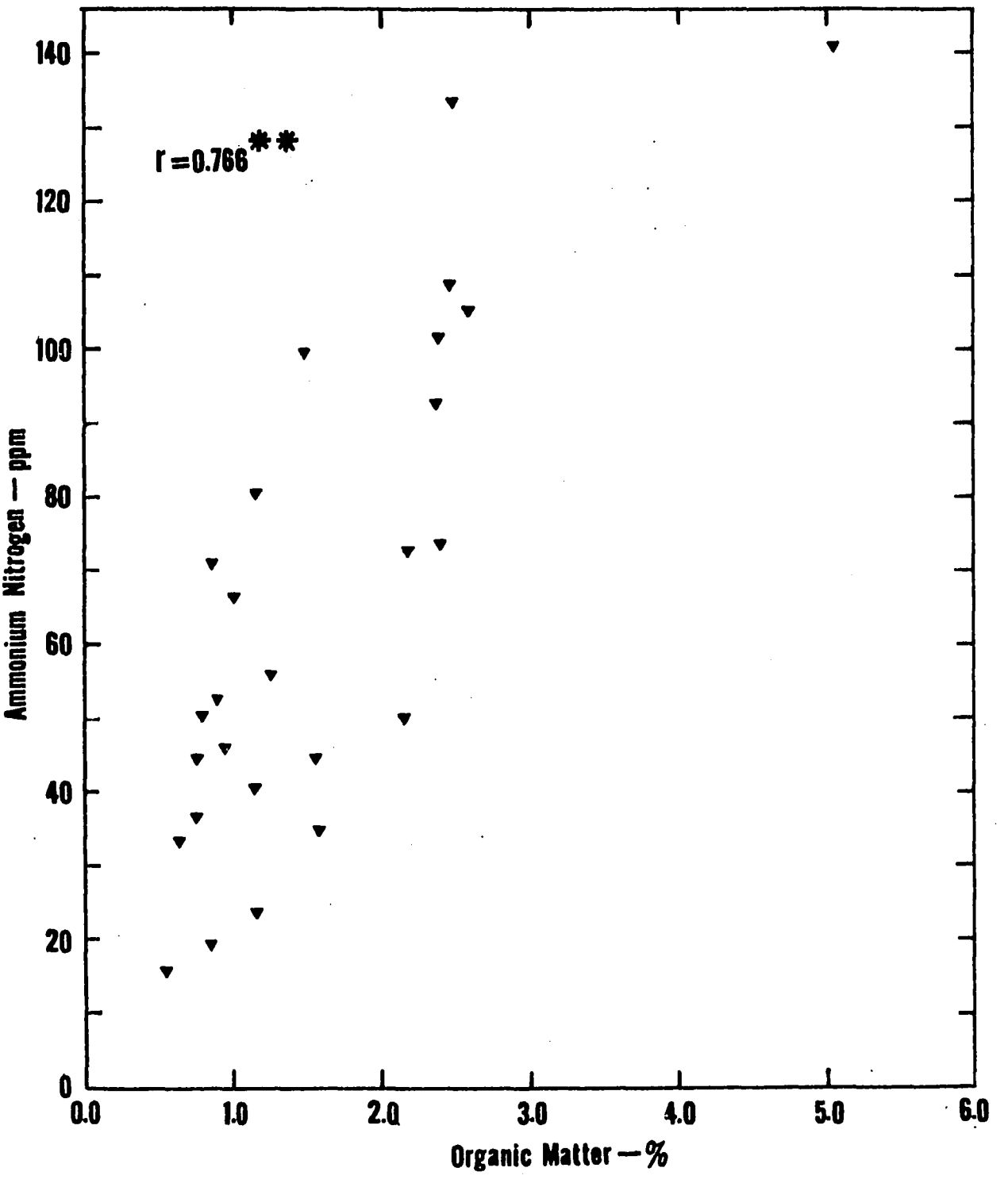


Figure 6. Correlation between ammonia content of soils submerged 30 days and soil organic matter content.

Highly significant correlations were also found between ammonia and clay, ferrous iron, phosphorus, specific conductivity, carbon dioxide production and methane production, Table 14. It will suffice to say that most of these are probably indirect correlations. These properties and ammonia mineralization are probably each dependent on the organic matter content of the soil. The correlation of ammonia with phosphorus is probably due to the fact that both are simultaneously mineralized under submerged conditions.

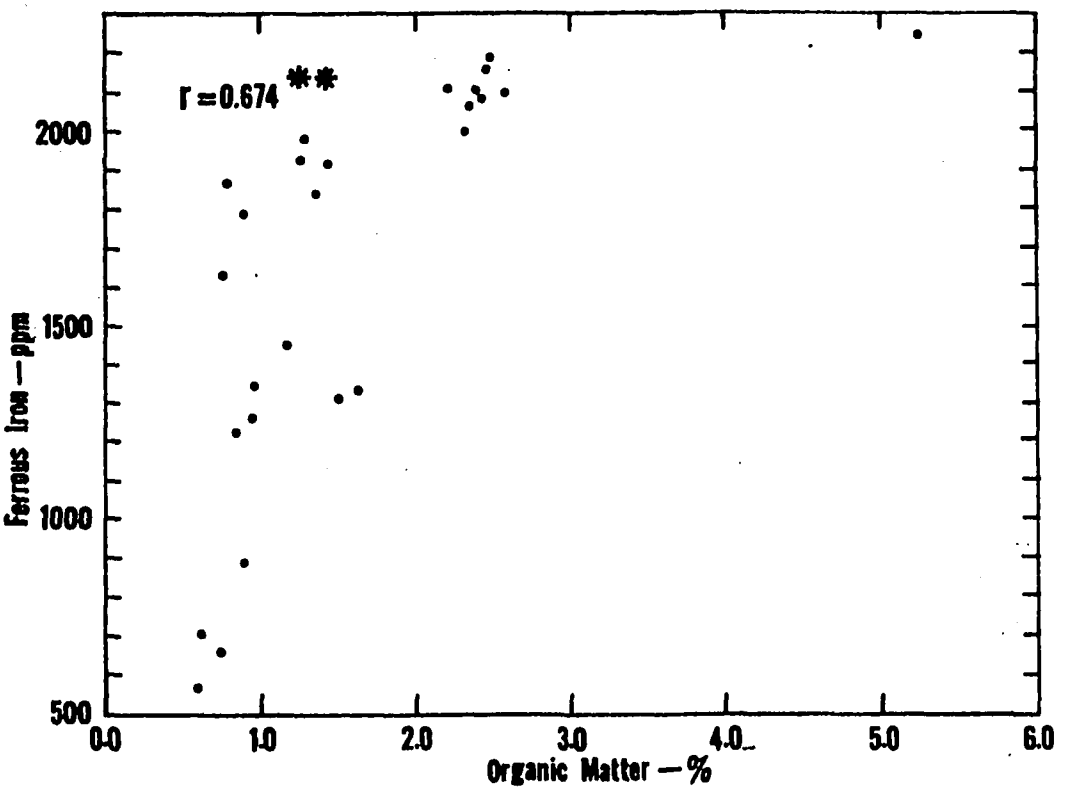
Iron Reduction.

Since it was found that under flooded conditions nearly all of the extractable iron was present in the ferrous form, the results reported in Table 6 are for ferrous iron.

Reference to Table 2 shows that initially the total iron (ferrous plus ferric) ranged from 3.3 parts per million in the Crowley silt loam (soil #18) to 18.7 parts per million in the Iberia clay (soil #26). Reference to Table 6 shows that initially the ferrous iron ranged from 2.3 parts per million in the Crowley silt loam (soil #18) to 8.2 parts per million in the Sharkey clay (soil #5). These values are insignificant in comparison with those of the submerged soils tabulated in Table 6. Under submerged conditions ferrous iron concentrations varied from 567 parts per million in the Yahola sandy loam (soil #12) to 2231 parts per million in the Sharkey clay (soil #5). Table 14 indicates that the ferrous iron concentration after submergence was positively correlated with clay and organic matter with r values of 0.625 and 0.674 respectively. Figure 7 illustrates the relationship between the final ferrous iron concentrations and the organic matter

Table 6. Extractable ferrous iron as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		Parts per million of ferrous iron					
			Initial	Flooded with No O.M. added	Flooded with O.M. added	Resulting from flooding	Resulting from flooding with O.M.	Difference due to O.M.
1	Commerce	l	6.9	1346	1346	1339	1339	0
2	Mhoon	sic	4.4	2105	2110	2101	2106	+ 5
3	Commerce	l	2.8	1632	1576	1629	1573	- 56
4	Mhoon	sicl	4.0	2110	2105	2106	2101	- 5
5	Sharkey	c	8.2	2231	2242	2223	2234	+ 11
6	Richland	sil	2.6	1255	1866	1252	1863	+611
7	Olivier	sil	3.2	1935	2025	1932	2022	+ 90
8	Lintonia	sil	3.7	1792	2003	1788	1999	+211
9	Gallion	sil	6.2	1211	1222	1205	1216	+ 11
10	Yahola	sil	4.8	661	722	656	717	+ 61
11	Miller	sic	3.4	1992	1958	1983	1955	- 34
12	Yahola	sl	2.8	567	661	564	658	+ 94
13	Yahola	l	3.7	1335	1369	1331	1365	+ 34
14	Sharkey	cl	3.5	1442	1996	1438	1992	+554
15	Sharkey	sl	3.3	883	1016	880	1013	+133
16	Sharkey	sic	3.3	2078	2073	2075	2070	- 5
17	Sharkey	l	3.9	1830	1909	1826	1905	+ 79
18	Crowley	sil	2.3	1862	1934	1860	1932	+ 72
19	Baldwin	sicl	8.2	1988	2000	1980	1992	+ 12
20	Mhoon	sicl	4.2	2084	2062	2080	2058	- 22
21	Baldwin	sicl	6.8	2076	2054	2069	2047	- 22
22	Baldwin	sicl	4.7	2151	2128	2146	2123	- 23
23	Midland	sicl	5.2	1303	1303	1298	1298	0
24	Richland	sil	2.8	1906	1988	1903	1985	+ 82
25	Commerce	sl	5.0	700	700	695	695	0
26	Iberia	c	7.4	2176	2206	2169	2199	+ 30



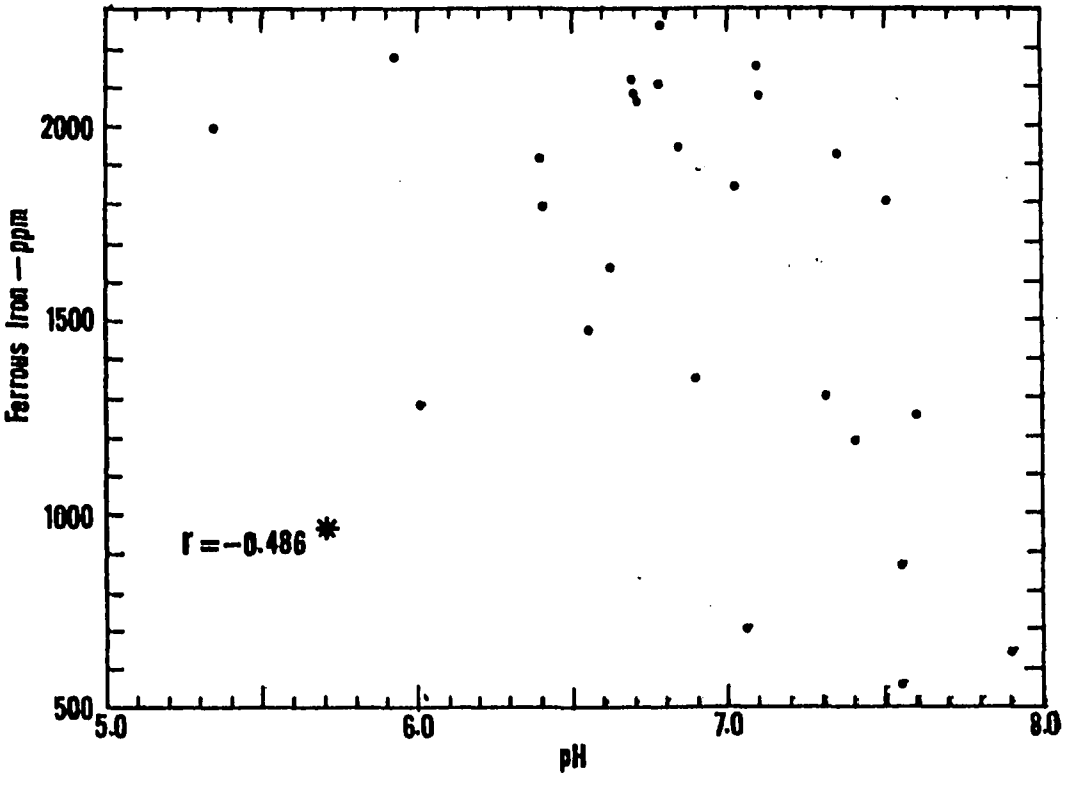


Figure 7. Correlation between extractable ferrous iron of soils submerged 30 days and soil organic matter content.

Figure 8. Correlation between extractable ferrous iron and pH of soils submerged 30 days.

contents of the soils. A similar relationship appeared before submergence ($r = 0.434$), as shown in Table 13, but this correlation was increased under submerged conditions. This may be interpreted as being due to more intensive reduction of oxidized forms of iron that function as election acceptors in biological reduction. This reduction is carried out by microorganisms in the presence of an energy source. This seems to be further substantiated by the fact that carbon dioxide production and methane production are positively correlated with the final ferrous iron concentrations with r values of 0.564 and 0.494, respectively, Table 14. Reduced organic products of microbial activity might have reduced ferric iron as suggested by Bloomfield (1953).

Ferrous iron was not consistently increased by adding 0.25 per cent ground corn leaves to the flooded soils. The effect of added organic matter ranged from an increase of 661 parts per million in the Richland silt loam (soil #6) to a decrease of 56 parts per million in the Commerce loam (soil #3). Generally, the results in Table 6 tend to indicate that added organic matter increased the amount of ferrous iron under flooded condition. This is also ascribed to the stimulative effect that organic matter had on the activities of the microorganisms responsible for reducing iron to the ferrous state. The decreases of ferrous iron under flooded conditions with added organic matter may have been due to ferrous iron being complexed with some organic fraction thereby diminishing the amount extracted. This decrease may also have been the result of the precipitation of ferrous and sulfide ions as ferrous sulfide.

Figure 8 illustrates the negative correlation between final ferrous iron concentrations and the pH of the submerged soils. This indicates that the more acid soils built up larger ferrous iron concentrations within 30 days of submergence than the less acid soils. A similar correlation existed before submergence with an r value of 0.435, as shown in Table 13, due to the hydrogen ion activity in the more acid soils. Larger ferrous iron concentrations after submergence are to be expected in the more acid soils since the higher hydrogen ion activity results in more iron being released from crystalline forms and being present in the soil as free iron oxide which is reducible under submerged conditions.

Ferrous iron concentrations were positively correlated with manganese and specific conductivity. There was no correlation between ferrous iron concentrations before flooding and after flooding, Table 15.

Changes in Extractable Phosphorus.

Most soils showed an increase in extractable phosphorus after submergence. The effect of flooding ranged from an increase of 392.9 parts per million phosphorus in the Sharkey clay (soil #5) to a decrease of 30.4 parts per million phosphorus in the Sharkey loam (soil #17), Table 7. There was a very close relationship between the amount of phosphorus extracted before submergence and after submergence ($r = 0.908$). The regression equation relating phosphorus extracted after submergence to phosphorus extracted before submergence showed that there was an average increase of 21 per cent in extractable

Table 7. Extractable phosphorus as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		Parts per million of phosphorus					
			Initial	Flooded with No O.M. added	Flooded with O.M. added	Resulting from flooding	Resulting from flooding with O.M.	Difference due to O.M.
1	Commerce	l	437.6	438.6	418.2	+ 1.0	- 19.4	- 18.4
2	Mhoon	sic	375.4	533.3	550.2	+117.9	+174.8	+ 56.9
3	Commerce	l	347.8	323.8	320.3	- 24.0	- 27.5	- 3.5
4	Mhoon	sicl	408.7	510.6	525.2	+101.9	+116.5	+ 14.6
5	Sharkey	c	425.1	818.0	818.6	+392.9	+393.5	+ 0.6
6	Richland	sil	105.6	165.6	192.9	+ 60.6	+ 87.9	+ 27.3
7	Olivier	sil	195.3	316.7	358.5	+121.4	+163.2	+ 41.8
8	Lintonia	sil	96.4	125.5	167.3	+ 29.1	+ 70.9	+ 41.8
9	Gallion	sil	148.0	151.5	155.0	+ 3.5	+ 7.0	+ 3.5
10	Yahola	sil	312.1	282.8	282.8	- 29.3	- 29.3	0.0
11	Miller	sic	344.9	386.4	386.9	+ 41.5	+ 42.0	+ 0.5
12	Yahola	sl	262.6	247.4	248.5	- 15.2	- 14.1	+ 1.1
13	Yahola	l	327.9	347.8	216.2	+ 19.9	-111.7	- 91.8
14	Sharkey	cl	321.4	319.3	344.2	- 2.1	+ 22.8	+ 24.9
15	Sharkey	sl	344.4	344.4	334.3	0.0	- 10.1	- 10.1
16	Sharkey	sic	245.7	347.6	347.6	+101.9	+101.9	0.0
17	Sharkey	l	378.0	347.6	365.6	- 30.4	- 12.4	+ 18.0
18	Crowley	sil	6.1	12.1	17.2	+ 6.0	+ 11.1	+ 5.1
19	Baldwin	sicl	52.5	91.2	99.9	+ 38.7	+ 47.4	+ 8.7
20	Mhoon	sicl	769.6	995.4	1047.0	+225.8	+277.4	+ 51.6
21	Baldwin	sicl	381.7	634.9	638.6	+253.2	+256.9	+ 3.7
22	Baldwin	sicl	267.3	439.9	450.8	+172.6	+183.5	+ 10.9
23	Midland	sicl	46.4	54.6	75.7	+ 8.2	+ 29.3	+ 21.1
24	Richland	sil	42.0	87.9	117.7	+ 45.9	+ 75.7	+ 29.8
25	Commerce	sl	393.9	394.9	385.8	+ 1.0	- 8.1	- 9.1
26	Iberia	c	75.2	178.8	200.6	+103.6	+125.4	+ 21.8

phosphorus due to submergence, Figure 9. This general increase in extractable phosphorus as a result of submergence is important in the phosphorus nutrition of lowland rice. The amount of phosphorus released after submergence was affected by the organic matter content of the soil, since a highly significant correlation existed between phosphorus after flooding and organic matter, Figure 10. This was probably due to its role in the reductive processes which occur. The highly significant and meaningful correlation (R = 0.749) between changes in ferrous iron and extractable phosphorus shown in Figure 11 is exponential in nature. This provides evidence that phosphorus is made more available through the mechanism of the reduction of ferric phosphate to ferrous phosphate. The release of ferrous iron had no effect on the release of phosphate until a value of extractable ferrous iron of approximately 1800 parts per million was reached. An increase in the release of iron beyond this point produced a marked release of phosphate.

Manganese Reduction.

Manganese concentrations were markedly increased after flooding, Table 8. These increases ranged from 33.6 parts per million manganese for the Commerce sandy loam (soil #25) to 1296 parts per million manganese in the Olivier silt loam (soil #7). This increase was due to the reduction of manganese as a consequence of the anaerobic metabolisms of soil bacteria. Similarly to ferric iron compounds, manganic compounds act as biological electron acceptors and are reduced to the more soluble manganous forms. Also, similarly to ferric compounds, manganese may be reduced chemically by organic compounds produced

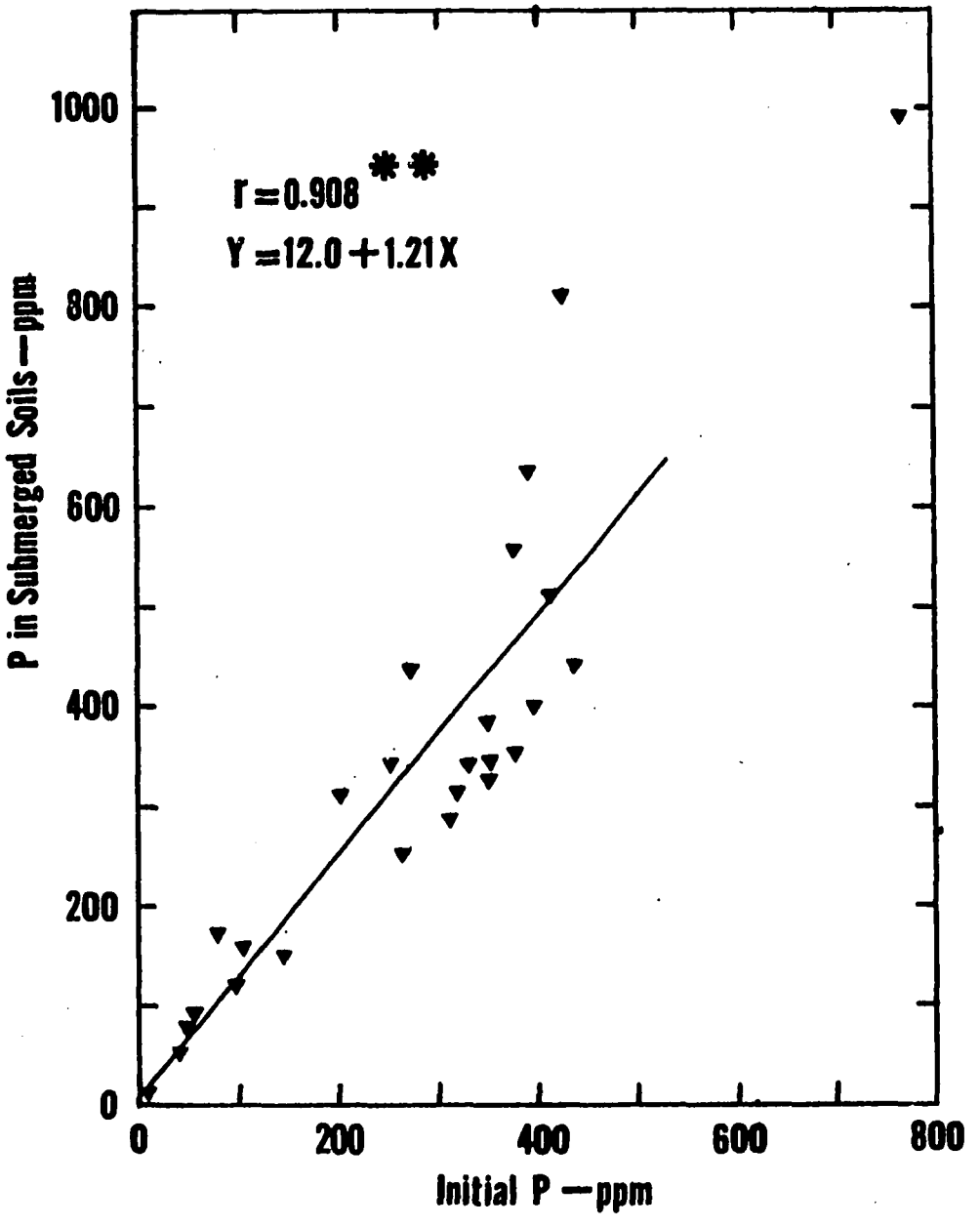


Figure 9. Relationship between extractable phosphorus of soils submerged 30 days and extractable phosphorus before submergence.

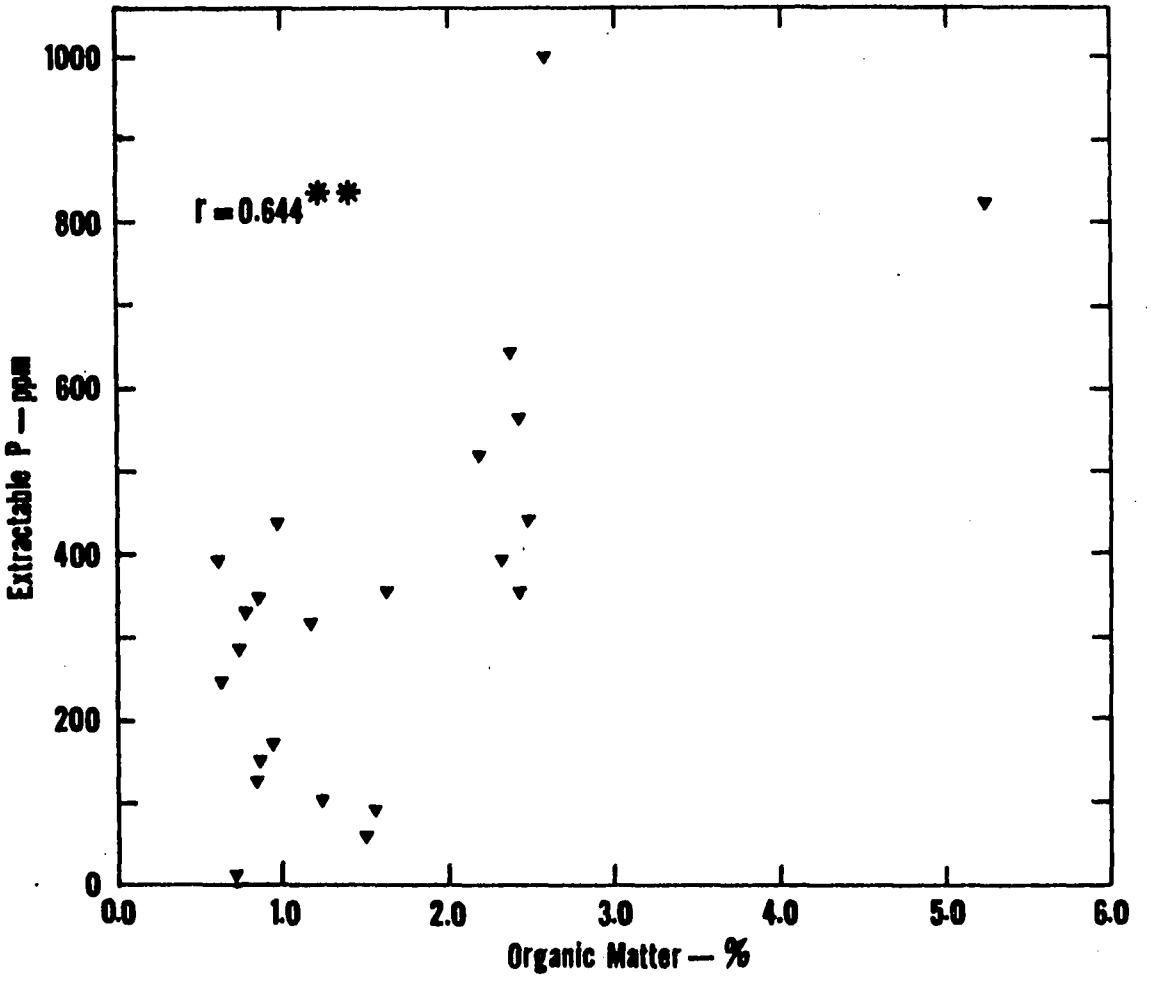


Figure 10. Correlation between extractable phosphorus of soils submerged 30 days and soil organic matter content.

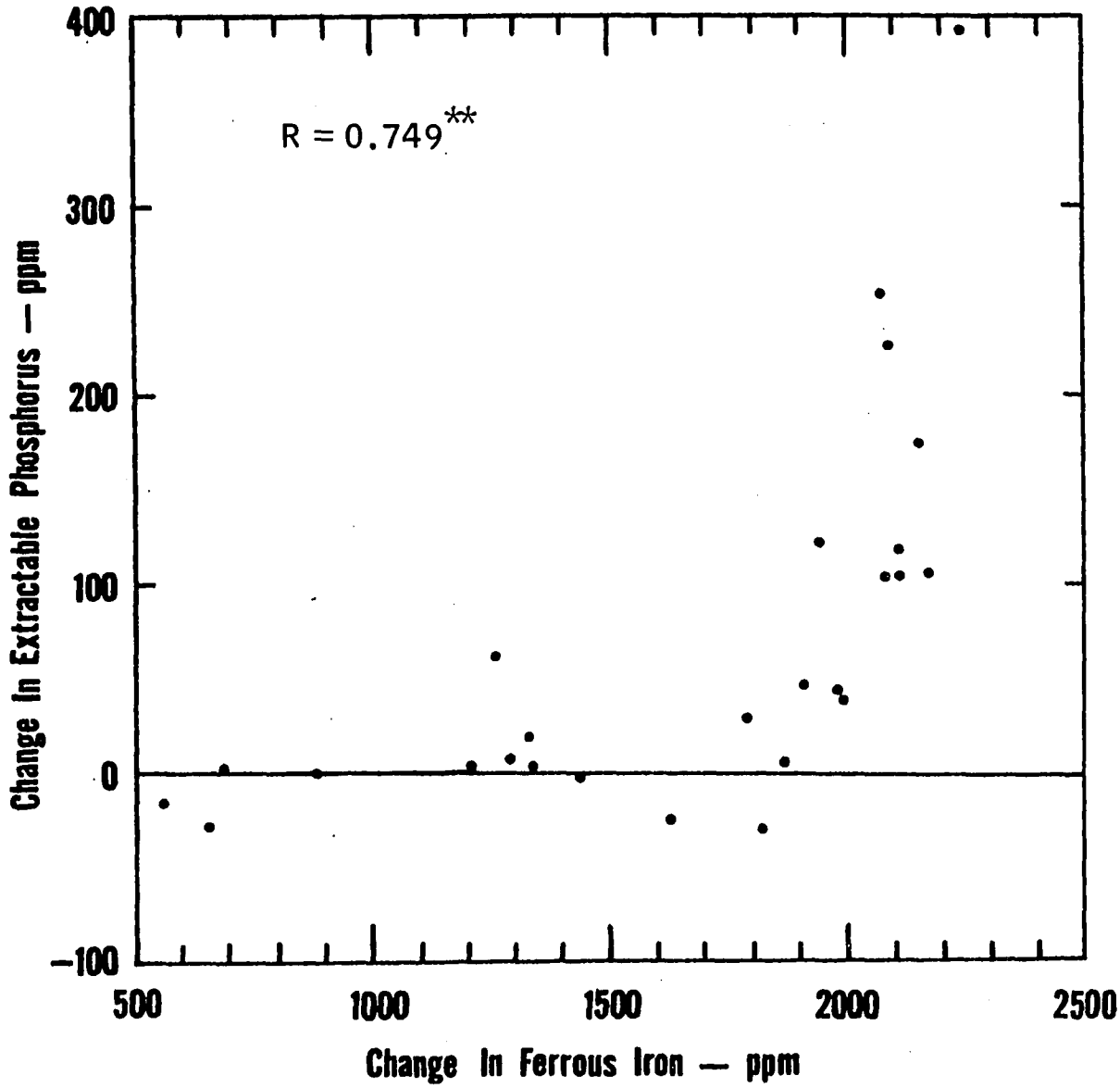


Figure 11. Correlation between change in extractable phosphorus and change in extractable ferrous iron of soils submerged 30 days.

Table 8. Extractable manganese as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		Parts per million of manganese					
			Initial	Flooded with No O.M. added	Flooded with O.M. added	Resulting from flooding	Resulting from flooding with O.M.	Difference due to O.M.
1	Commerce	l	40.1	81.9	76.9	41.8	36.8	- 5.0
2	Mhoon	sic	83.8	490.8	490.8	407.0	407.0	0.0
3	Commerce	l	37.9	116.1	114.4	78.2	76.5	- 1.7
4	Mhoon	sicl	74.5	383.0	408.3	308.5	333.8	+ 25.3
5	Sharkey	c	76.3	441.2	470.0	364.9	393.7	+ 28.8
6	Richland	sil	159.4	1400	1732	1241	1572	+331
7	Olivier	sil	87.9	1384	1500	1296	1412	+115
8	Lintonia	sil	58.1	464.5	508.8	406.4	450.7	+ 44.3
9	Gallion	sil	16.4	103.9	102.8	87.5	86.4	- 1.1
10	Yahola	sil	44.1	88.9	101.7	44.8	57.6	+ 12.8
11	Miller	sic	59.3	475.9	473.6	416.6	414.6	- 2.0
12	Yahola	sl	21.2	85.0	87.8	63.8	66.6	+ 2.8
13	Yahola	l	57.7	237.9	242.9	180.2	185.2	+ 5.0
14	Sharkey	cl	49.8	415.8	462.8	366.0	413.0	+ 47.0
15	Sharkey	sl	20.5	151.6	152.8	131.1	132.3	+ 1.2
16	Sharkey	sic	75.2	604.1	615.6	528.9	540.4	+ 11.5
17	Sharkey	l	66.0	219.8	224.9	153.8	158.9	+ 5.1
18	Crowley	sil	126.6	548.3	571.1	421.7	444.5	+ 22.8
19	Baldwin	sicl	34.5	158.6	95.7	124.1	61.2	- 62.9
20	Mhoon	sicl	129.7	566.4	577.5	436.7	447.8	+ 11.1
21	Baldwin	sicl	123.8	765.3	657.8	641.5	534.0	-107.5
22	Baldwin	sicl	116.0	612.0	599.5	496.0	483.5	- 12.5
23	Midland	sicl	76.2	116.7	116.7	40.5	40.5	0.0
24	Richland	sil	171.0	766.6	748.8	595.6	577.8	- 17.8
25	Commerce	sl	28.1	61.7	55.6	33.6	27.5	- 6.1
26	Iberia	c	42.6	223.0	254.8	180.4	212.2	+ 31.8

during the anaerobic decomposition of organic matter as suggested by Mann and Quastel (1946). The striking feature with manganese was that its concentration after flooding was closely related to the manganese content before flooding. The correlation coefficient (r) between the initial manganese concentrations and the concentrations 30 days after submergence was 0.755 (Table 15), and the equation relating these two was $Y = -39.7 + 6.39X$ where Y is the estimated concentration after flooding and X the concentration before flooding. This relationship is illustrated in Figure 12. The regression coefficient shows that there was an average six-fold increase in extractable manganese as a result of submergence.

The effect of added organic matter was inconsistent, ranging from an increase of 331 parts per million manganese in the Richland silt loam (soil #6) to a decrease of 107.5 parts per million in the Baldwin silty clay (soil #21), Table 8. An examination of the results in Table 8 shows that organic matter usually caused an increase in the concentration of manganese, although the relationship was not statistically significant. A probable reason as to why added organic matter did not more definitely affect manganese solubility may lie in the fact that manganese is very easily reduced under submerged conditions when compared to iron and additional organic matter is not necessary for manganese release. Manganese reduced to a more soluble form may be later tied up in a non-extractable form as a complex compounds.

There was a significant degree of association between manganese before submergence and ferrous iron after flooding ($r = 0.468$), Table

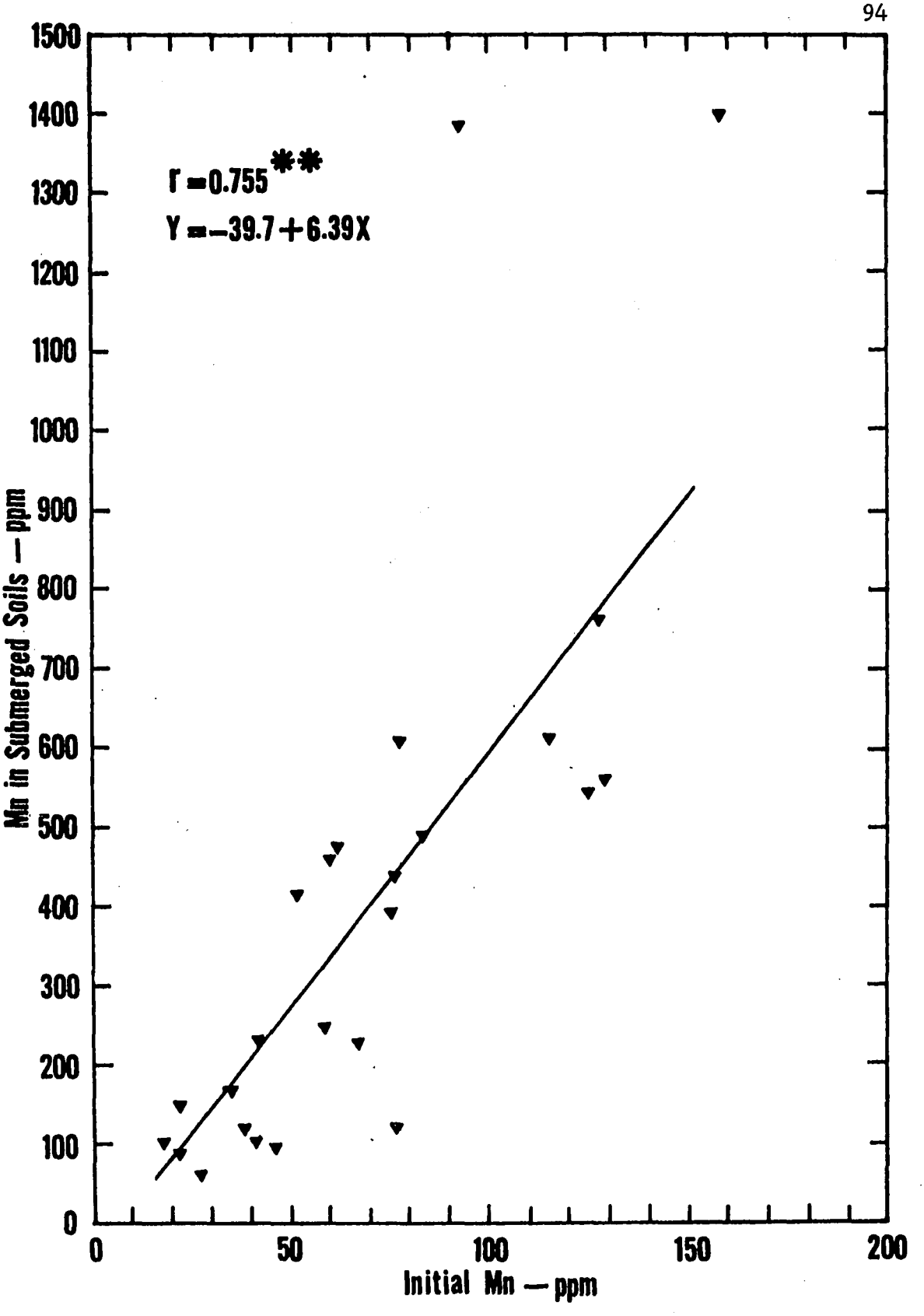


Figure 12. Relationship between extractable manganese of soils submerged 30 days and extractable manganese before submergence.

15, and also between manganese after submergence and ferrous iron after submergence ($r = 0.400$), in Table 14.

Changes in pH.

The pH values given in Table 9 show that flooding increased the pH of the soil as much as 1.60 pH units in 30 days for the acid Baldwin silty clay loam (soil #22). There were certain soils in which flooding produced the reverse effect, viz. a reduction in pH after flooding. These were six non-acid soils with pH's ranging from 6.95 to 7.95. The increase in pH from submergence was probably due to the hydrolysis of minerals containing calcium and magnesium and the production of hydroxide ions as a result of the reduction of ferric hydroxide or hydrated ferric oxide.

The tendency for soils of low pH to increase in pH and for soils of high pH to decrease in pH upon submergence suggests that the pH of submerged soils tends to be buffered around neutrality by substances produced as a result of submergence. Because of the high release of ferrous iron and the buildup of carbon dioxide under submerged conditions, ferrous carbonate probably plays an important role in controlling the pH of submerged soils, "Soil Chemistry" (1963). The decrease in pH was confined to soils with initially high pH values. An explanation for this might well be that the acids (lactic and butyric) produced in the process of anaerobic fermentation were responsible for this decrease in pH. The carbon dioxide dissolved in the flood water would also tend to shift the pH to the acid side. Regardless of the mechanism involved the increase or decrease in pH as a result of submergence was related to the original pH of the

Table 9. Soil pH as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		pH[1] Initial	Flooded with No O.M. added	Flooded with O.M. added	Resulting from flooding	Resulting from flooding with O.M.	Difference due to O.M.
1	Commerce	l	6.85	6.90	7.60	+0.05	+0.75	+0.70
2	Mhoon	sic	6.45	6.77	7.00	+0.32	+0.55	+0.23
3	Commerce	l	6.55	6.62	7.21	+0.07	+0.66	+0.59
4	Mhoon	sicl	6.60	6.69	6.99	+0.09	+0.39	+0.30
5	Sharkey	c	6.60	6.79	7.03	+0.19	+0.43	+0.24
6	Richland	sil	6.00	6.00	7.45	0.00	+1.45	+1.45
7	Olivier	sil	6.15	6.85	7.25	+0.70	+1.10	+0.40
8	Lintonia	sil	6.15	6.40	7.20	+0.25	+1.05	+0.80
9	Gallion	sil	6.10	7.40	7.49	+1.30	+1.39	+0.09
10	Yahola	sil	7.95	7.90	7.23	-0.05	-0.72	-0.67
11	Miller	sic	7.65	7.35	7.42	-0.30	-0.23	+0.07
12	Yahola	sl	7.90	7.55	7.65	-0.35	-0.25	+0.10
13	Yahola	l	7.90	7.60	7.25	-0.30	-0.65	+0.35
14	Sharkey	cl	6.95	6.55	7.11	-0.40	+0.16	+0.56
15	Sharkey	sl	7.67	7.55	7.48	-0.12	-0.22	+0.34
16	Sharkey	sic	6.05	6.70	7.05	+0.65	+1.00	+0.35
17	Sharkey	l	6.45	7.02	7.28	+0.57	+0.83	+0.26
18	Crowley	sil	6.85	7.50	7.50	+0.65	+0.65	0.00
19	Baldwin	sicl	4.85	5.35	6.50	+0.50	+1.65	+1.15
20	Mhoon	sicl	6.70	7.10	7.20	+0.40	+0.50	+0.10
21	Baldwin	sicl	5.20	6.69	6.95	+1.49	+1.75	+0.26
22	Baldwin	sicl	5.50	7.10	6.99	+1.60	+1.49	-0.11
23	Midland	sicl	6.65	7.31	7.06	+0.66	+0.41	-0.25
24	Richland	sil	5.65	6.40	7.50	+0.75	+1.85	+1.10
25	Commerce	sl	6.50	7.06	7.51	+0.56	+1.01	+0.45
26	Iberia	c	5.20	5.94	6.80	+0.74	+1.60	+0.86

[1]One to one ratio of air-dry soil to distilled water.

soil, Figure 13. This relationship had a correlation coefficient of 0.777. An analysis of the regression equation shows that on the average, soils with original pH values above 7.4 decreased in pH after submergence and soils with original pH value below 7.4 increased in pH after submergence. The average increase or decrease was 0.53 pH units for each pH unit below or above pH 7.4.

The data of Table 9 show that organic matter generally favored the development of higher alkalinity. These increases in pH are probably the result of an accelerated reduction process which liberated iron and manganese in reduced forms. In a few cases a decrease in pH resulted from adding organic matter. This may have resulted from large amounts of carbon dioxide and organic acids being produced under anaerobic conditions.

Figures 14a to 14z illustrate the pH values of submerged soils at monthly intervals, for four months, for the 26 soils both with and without organic matter added. Generally, the pH increased with duration of submergence and then decreased. The tendency seemed for pH values to become more or less stable after a few months irrespective of the presence or absence of added organic matter. The fluctuations appeared to be associated with initial pH, organic matter content, and ferrous iron and manganese fluctuations. The initial increase followed by a decrease in pH indicates that acid neutralizing substances such as ferrous iron and manganous manganese are first released and then precipitated or complexed out of solution. In this respect it has recently found that in latosolic acid soils variations in alkalinity

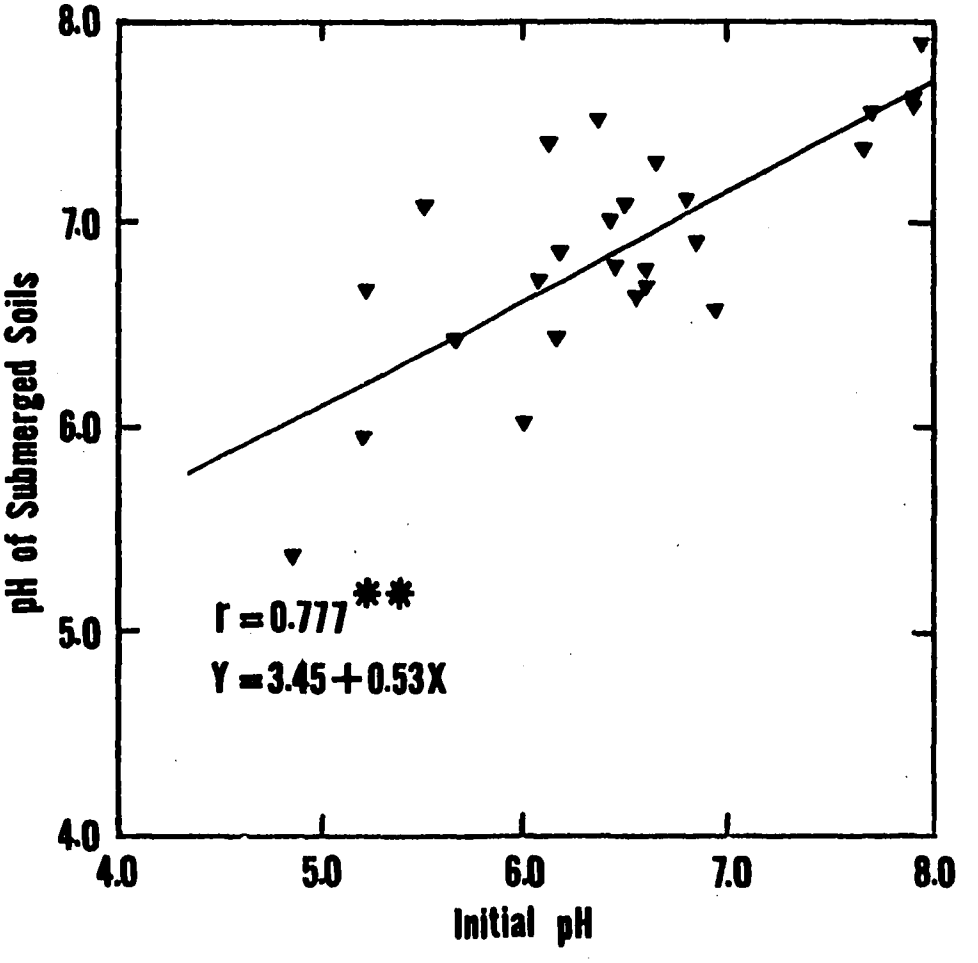
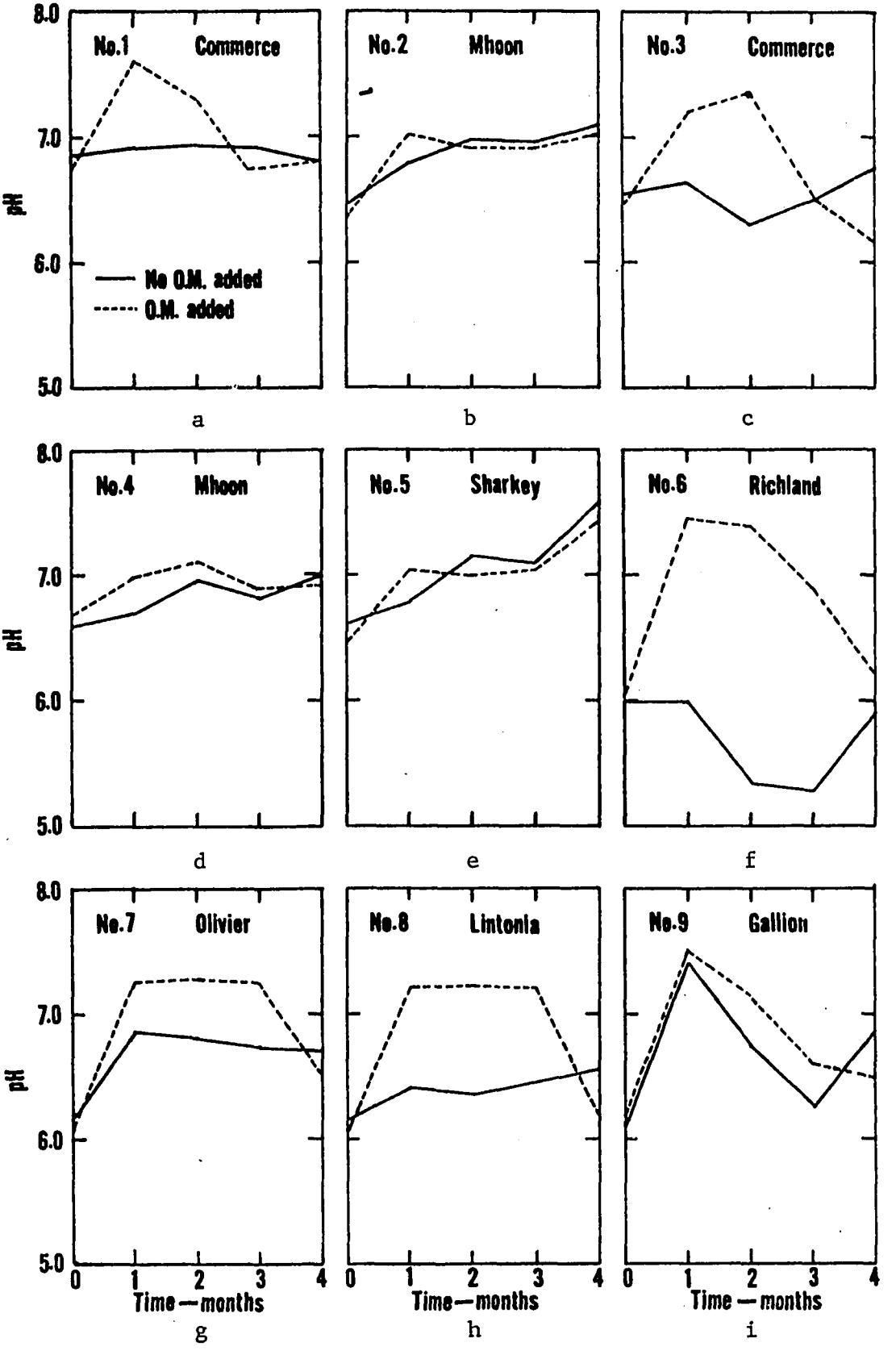
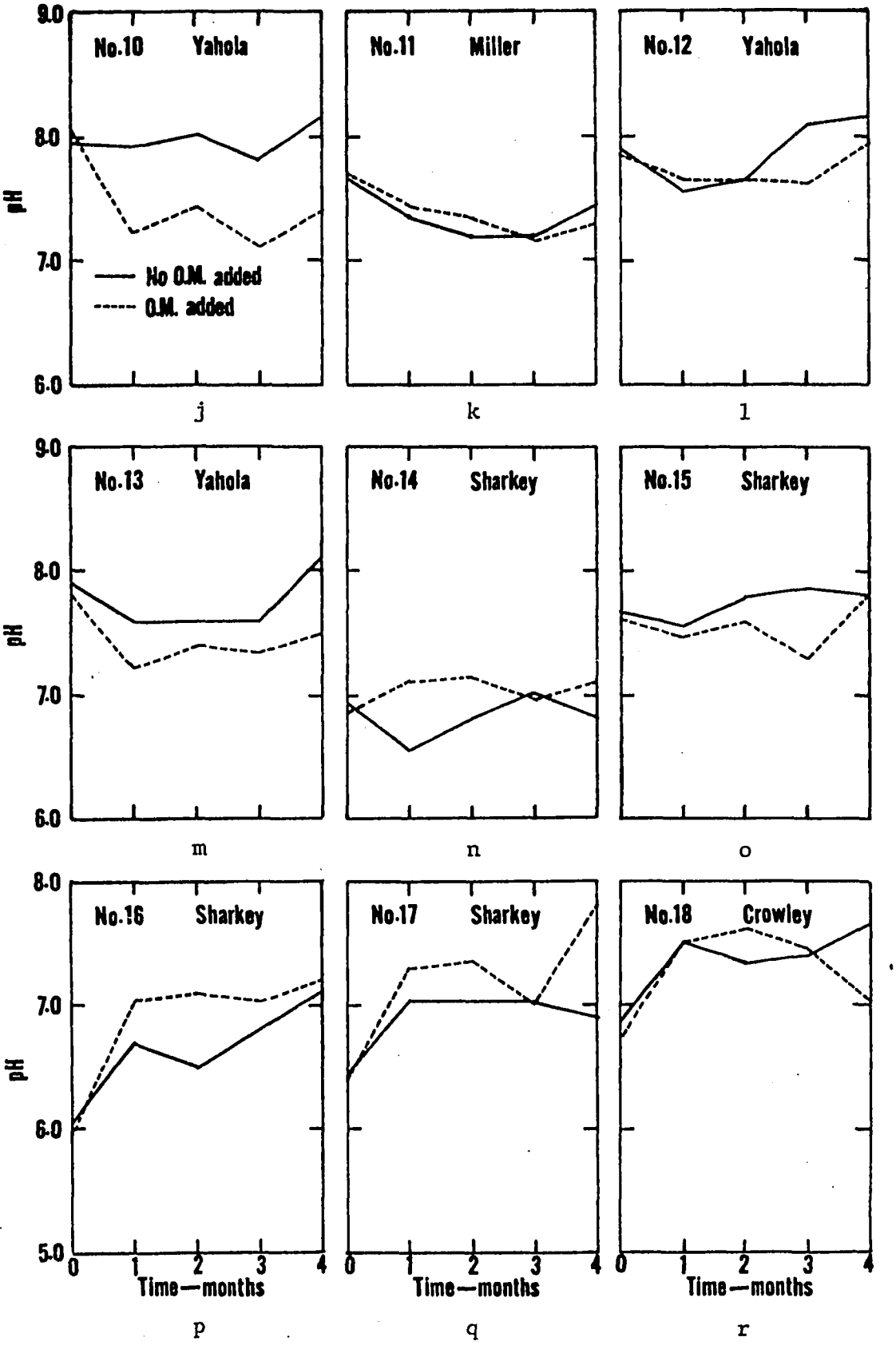


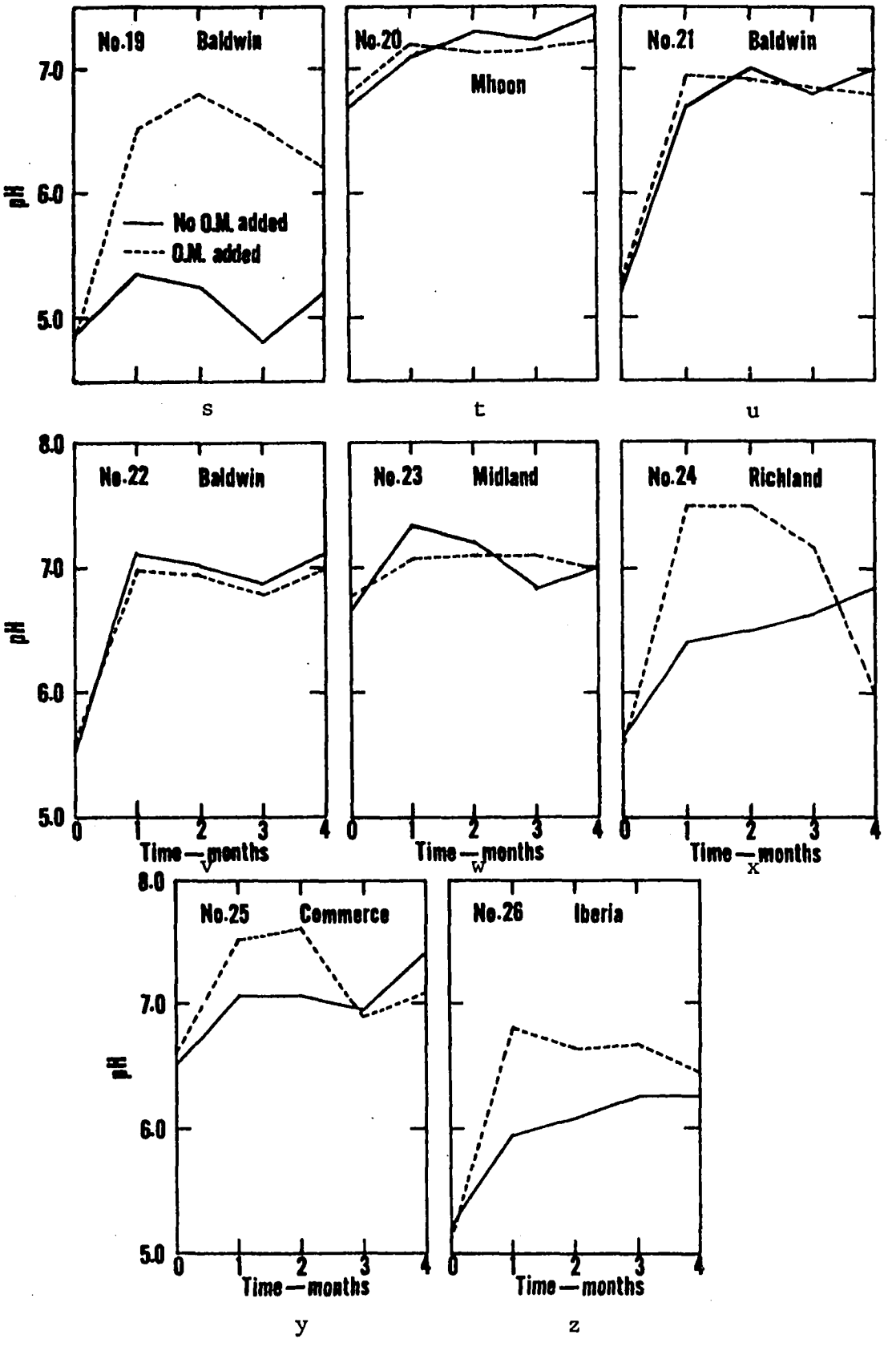
Figure 13. Relationship between pH of soils submerged 30 days and pH before submergence.



Figures 14a-14i. Changes in soil pH after submergence with and without added organic matter.



Figures 14j-14r. Changes in soil pH after submergence with and without added organic matter.



Figures 14s-14z. Changes in soil pH after submergence with and without added organic matter.

were roughly parallel to soluble ferrous iron, while in calcareous soils the mobilization of calcium and magnesium was the influencing factor, "Soil Chemistry" (1963).

Changes in Specific Conductivity.

Specific conductivity of one to one soil to water suspensions are shown in Table 10. Flooding increased the specific conductivity of all the soils with the exception of the Sharkey silty clay (soil #16) and the Richland silt loam (soil #24). Specific conductivity per se is a measure of ionic activity or concentration. Increases in specific conductivity therefore reflected increases in ionic concentrations. The correlation coefficients in Table 14 reflect the fact that specific conductivity was positively highly significantly correlated with clay, organic matter, ammonia, ferrous iron, phosphorus, carbon dioxide production and methane production. The correlations with organic matter, carbon dioxide production and methane production were probably due to organic matter enhancing bacterial activity thereby accelerating the solubility of the reduction products. The relationship between organic matter and specific conductivity is illustrated in Figure 15. Table 13 shows a highly significant correlation ($r = 0.754$) between initial specific conductivity and initial nitrate nitrogen concentration. The two soils which decreased in specific conductivity upon submergence were originally the highest in nitrate nitrogen concentration. Obviously, the decrease in specific conductivity of these two soils after submergence caused by the loss of nitrate nitrogen through denitrification was not compensated for

Table 10. Soil specific conductivity as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

No.	Soil		Specific conductivity - mmhos per cm.[1] Initial	Flooded with No O.M. added	Flooded with O.M. added	Difference due to flooding	Difference due to flooding with O.M.	Difference due to added O.M.
1	Commerce	l	0.190	0.200	0.693	+0.10	+0.503	+0.493
2	Mhoon	sic	0.338	0.965	1.802	+0.627	+1.464	+0.837
3	Commerce	l	0.148	0.208	0.901	+0.060	+0.753	+0.693
4	Mhoon	sicl	0.392	0.772	1.081	+0.380	+0.689	+0.309
5	Sharkey	c	0.772	1.351	1.802	+0.579	+1.630	+0.451
6	Richland	sil	0.129	0.284	0.540	+0.155	+0.411	+0.256
7	Olivier	sil	0.165	0.416	0.772	+0.251	+0.607	+0.356
8	Lintonia	sil	0.125	0.186	0.676	+0.063	+0.553	+0.490
9	Gallion	sil	0.136	0.318	0.601	+0.182	+0.465	+0.283
10	Yahola	sil	0.270	0.386	0.901	+0.116	+0.631	+0.515
11	Miller	sic	0.450	0.845	1.081	+0.395	+0.631	+0.236
12	Yahola	sl	0.229	0.318	0.676	+0.089	+0.447	+0.358
13	Yahola	l	0.351	0.540	1.081	+0.189	+0.730	+0.541
14	Sharkey	cl	0.294	0.416	1.502	+0.122	+1.208	+1.086
15	Sharkey	sl	0.211	0.284	0.711	+0.073	+0.500	+0.427
16	Sharkey	sic	0.872	0.676	1.351	-0.196	+0.479	+0.675
17	Sharkey	l	0.273	0.416	0.901	+0.143	+0.628	+0.485
18	Crowley	sil	0.257	0.416	0.711	+0.159	+0.454	+0.295
19	Baldwin	sicl	0.284	0.540	0.772	+0.256	+0.488	+0.232
20	Mhoon	sicl	0.520	0.901	1.228	+0.381	+0.708	+0.327
21	Baldwin	sicl	0.520	0.901	1.228	+0.381	+0.708	+0.327
22	Baldwin	sicl	0.375	0.901	1.351	+0.526	+0.976	+0.450
23	Midland	sicl	0.300	0.540	0.901	+0.240	+0.601	+0.361
24	Richland	sil	0.397	0.300	1.081	-0.097	+0.683	+0.780
25	Commerce	sl	0.222	0.225	0.772	+0.003	+0.550	+0.547
26	Iberia	c	0.552	1.081	1.502	+0.529	+0.950	+0.421

[1]One to one ratio of air-dry soil to distilled water.

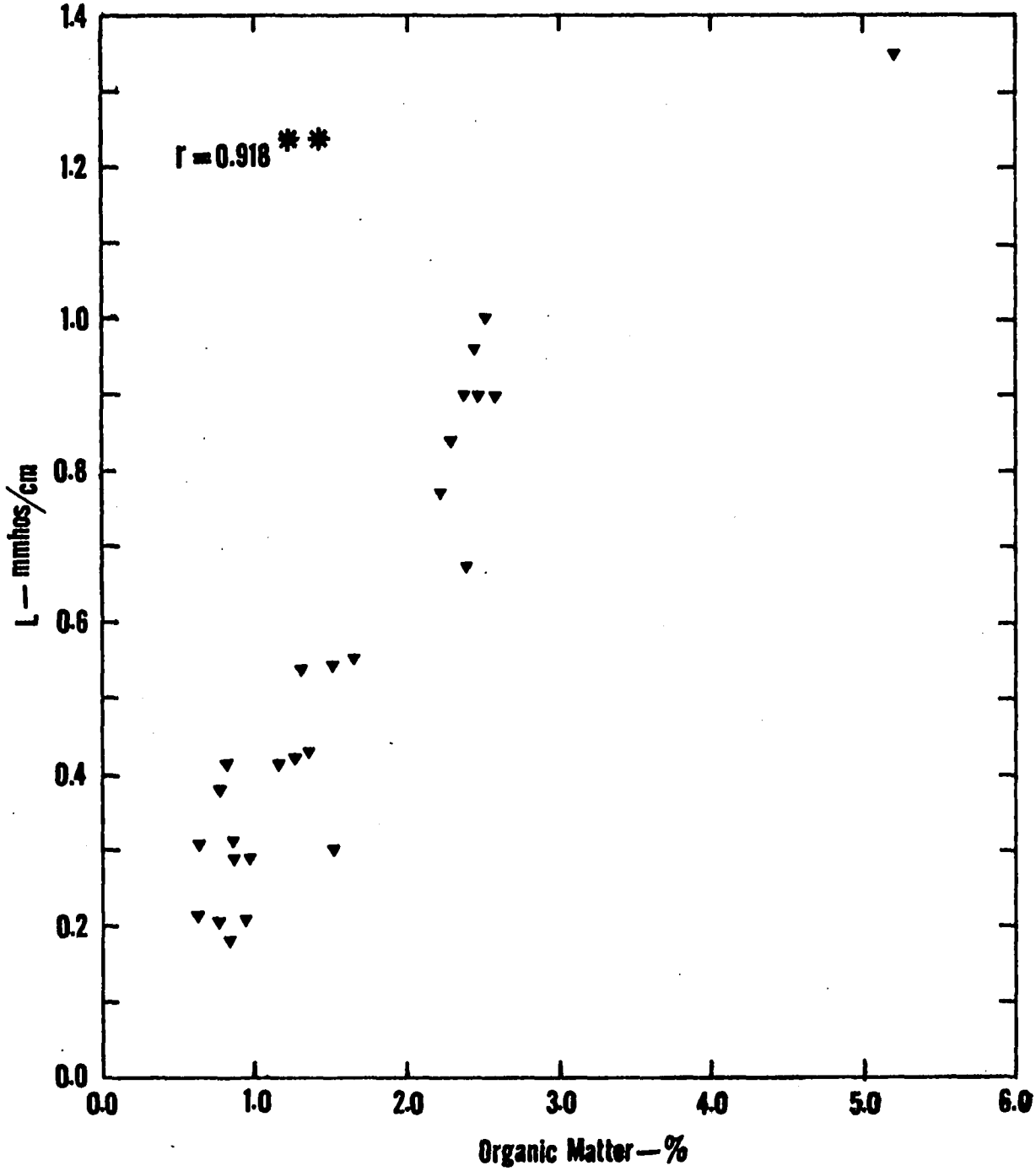


Figure 15. Correlation between specific conductivity of soils submerged 30 days and soil organic matter content.

by an increase in specific conductivity resulting from the increased solubility of reduction products.

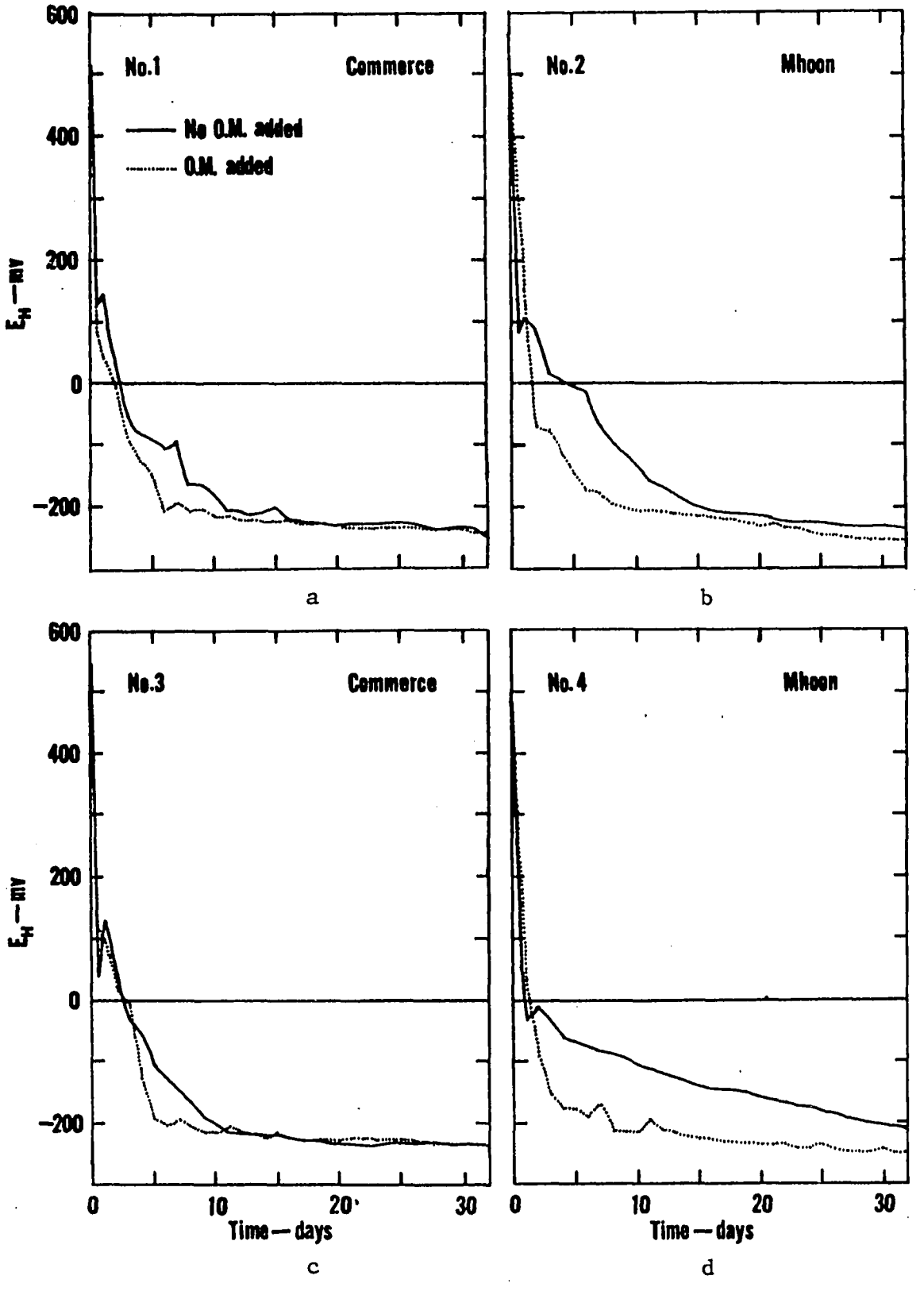
Adding 0.25 per cent ground corn leaves definitely increased the specific conductivity. This reflects the fact that organic matter augmented the production of soluble reduced products.

Noticeably, manganese concentrations after submergence were not significantly correlated with the specific conductivity after submergence.

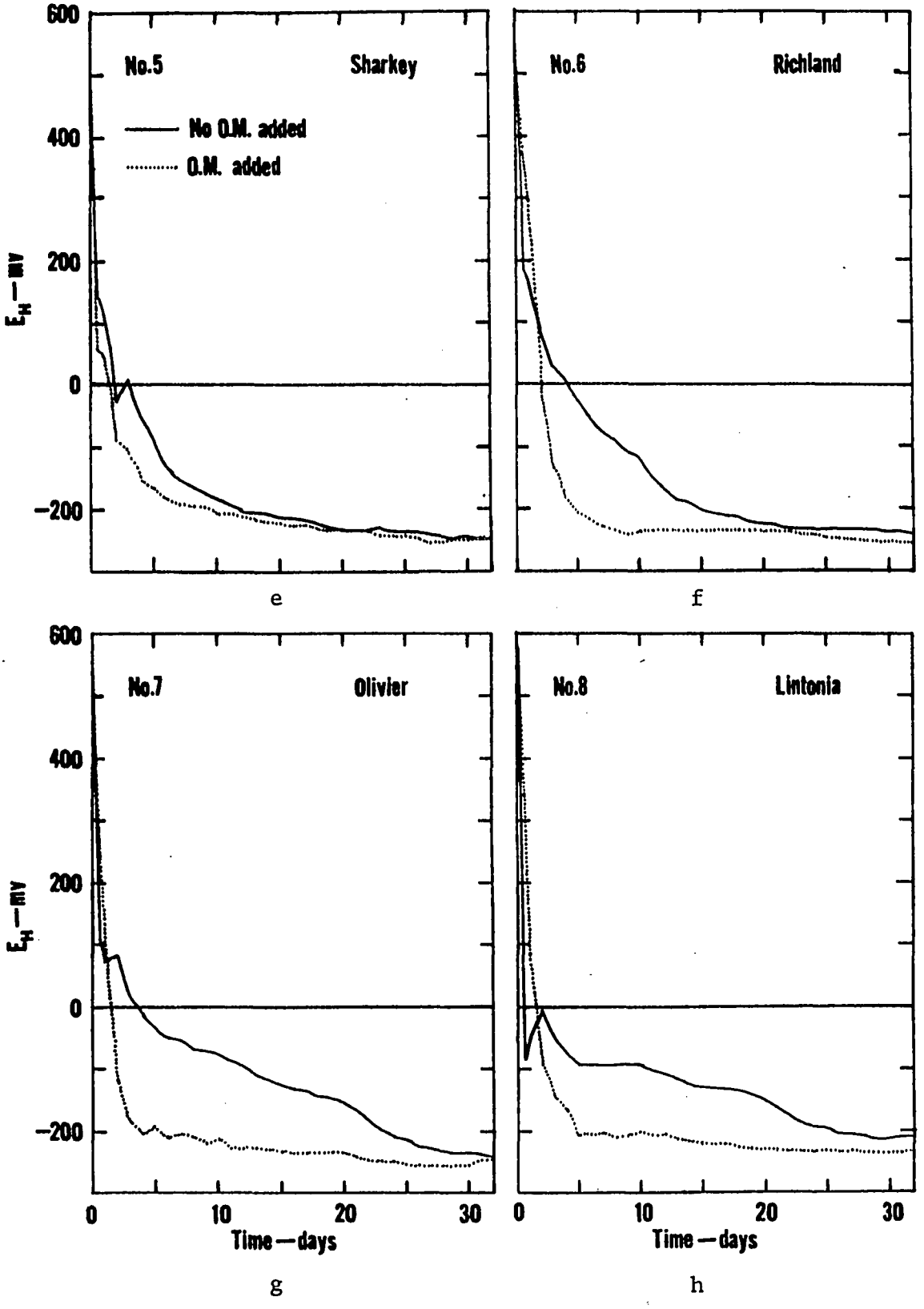
Changes in Redox Potential.

The redox potentials of the soils at various times after submergence are shown in Figures 16a to 16z. Readings taken immediately after submergence showed the redox potentials of the soils to range from +424 millivolts in the Yahola sandy loam (soil #12) to +634 millivolts in Baldwin silty clay loams (soil #19 and #21), Table 11. There was a close relationship between the redox potential taken a few minutes after submergence and the pH of the soil. This relationship is illustrated in Figure 17. The E_h/pH slope was -61.8 millivolts per pH unit. This is very close to the theoretical value of -60 millivolts per pH unit for the hydrogen system. Most of the variation in original redox potential was obviously due to differences in pH. Correcting these initial redox potential values to pH 7.0 by means of the regression equation shown in Figure 17 gives an average initial redox potential for all soils of +503 millivolts.

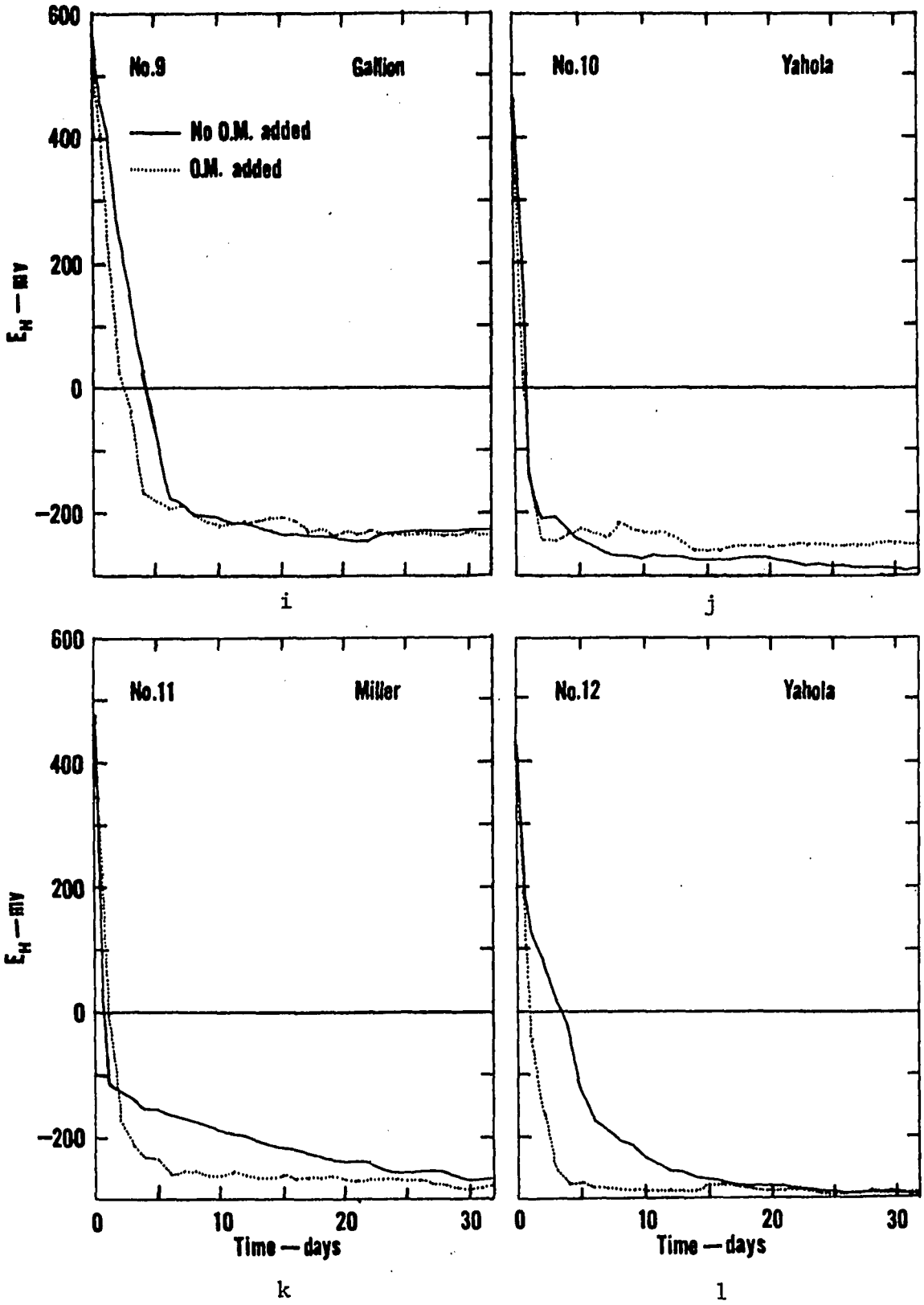
The potentials decreased sharply after submergence. In some soils this sharp decrease was followed by a temporary rise in potential. The rapid fall in potential followed by a temporary rise may have been



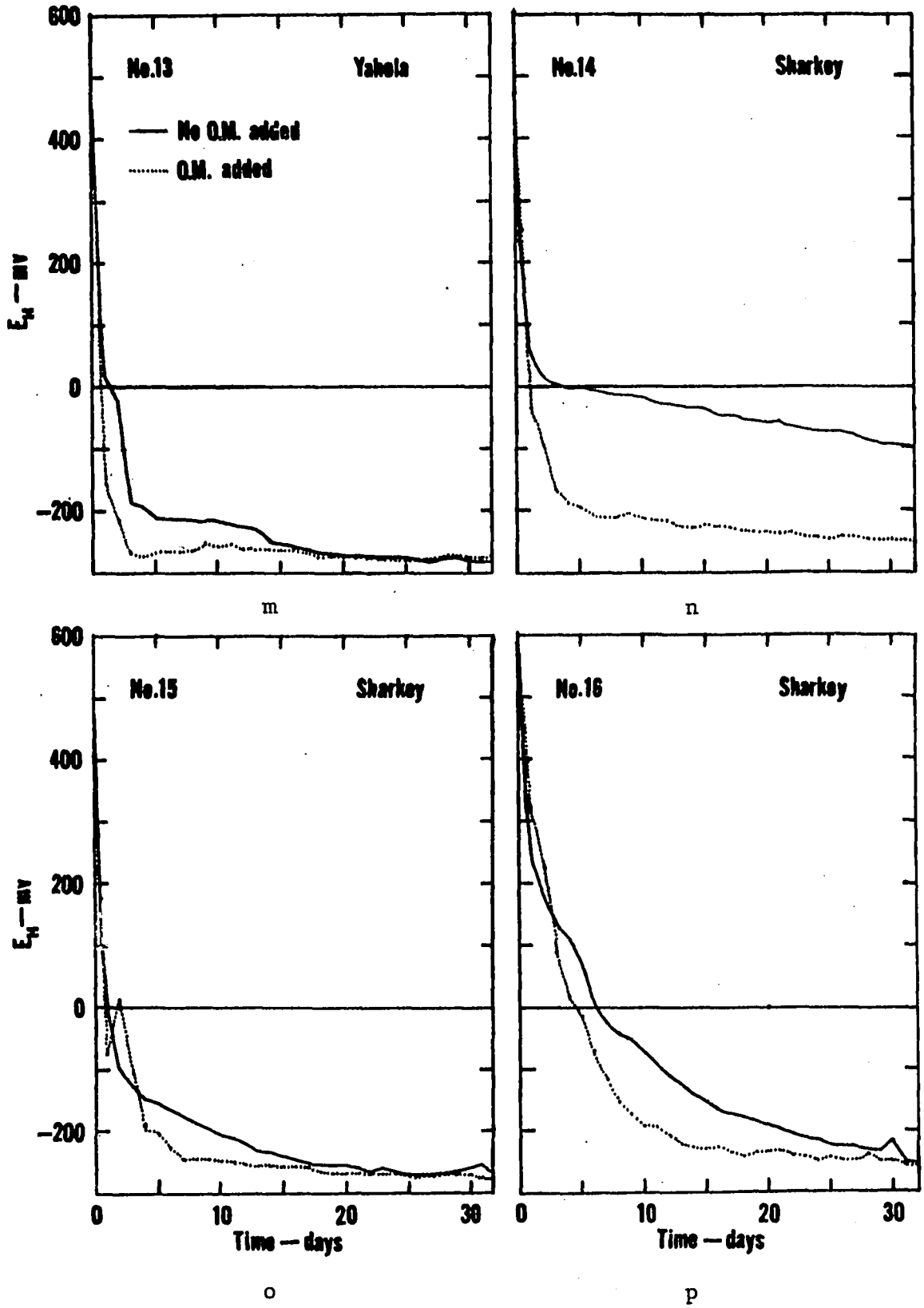
Figures 16a-16d. Changes in soil redox potential after submergence with and without added organic matter.



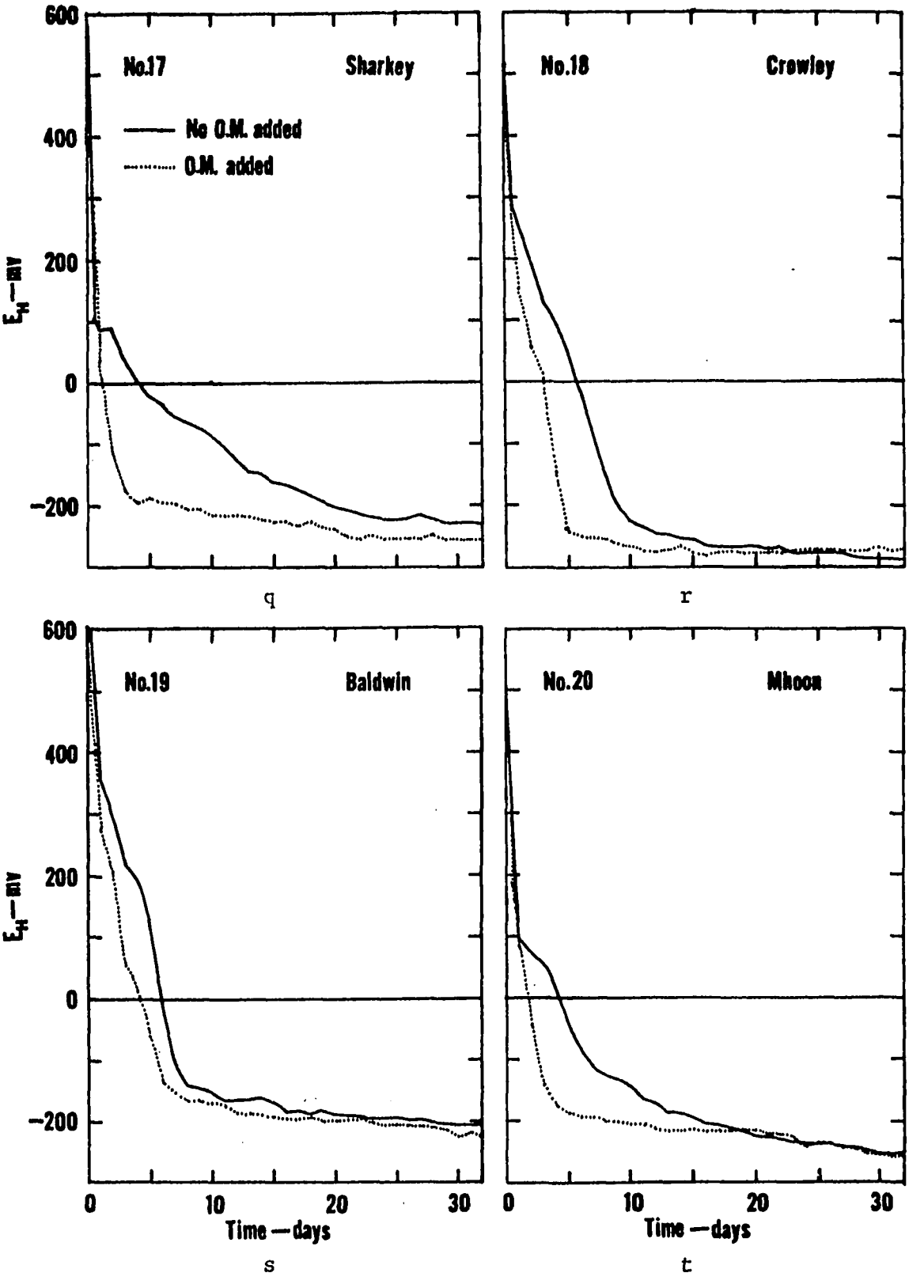
Figures 16e-16h. Changes in redox potential after submergence with and without added organic matter.



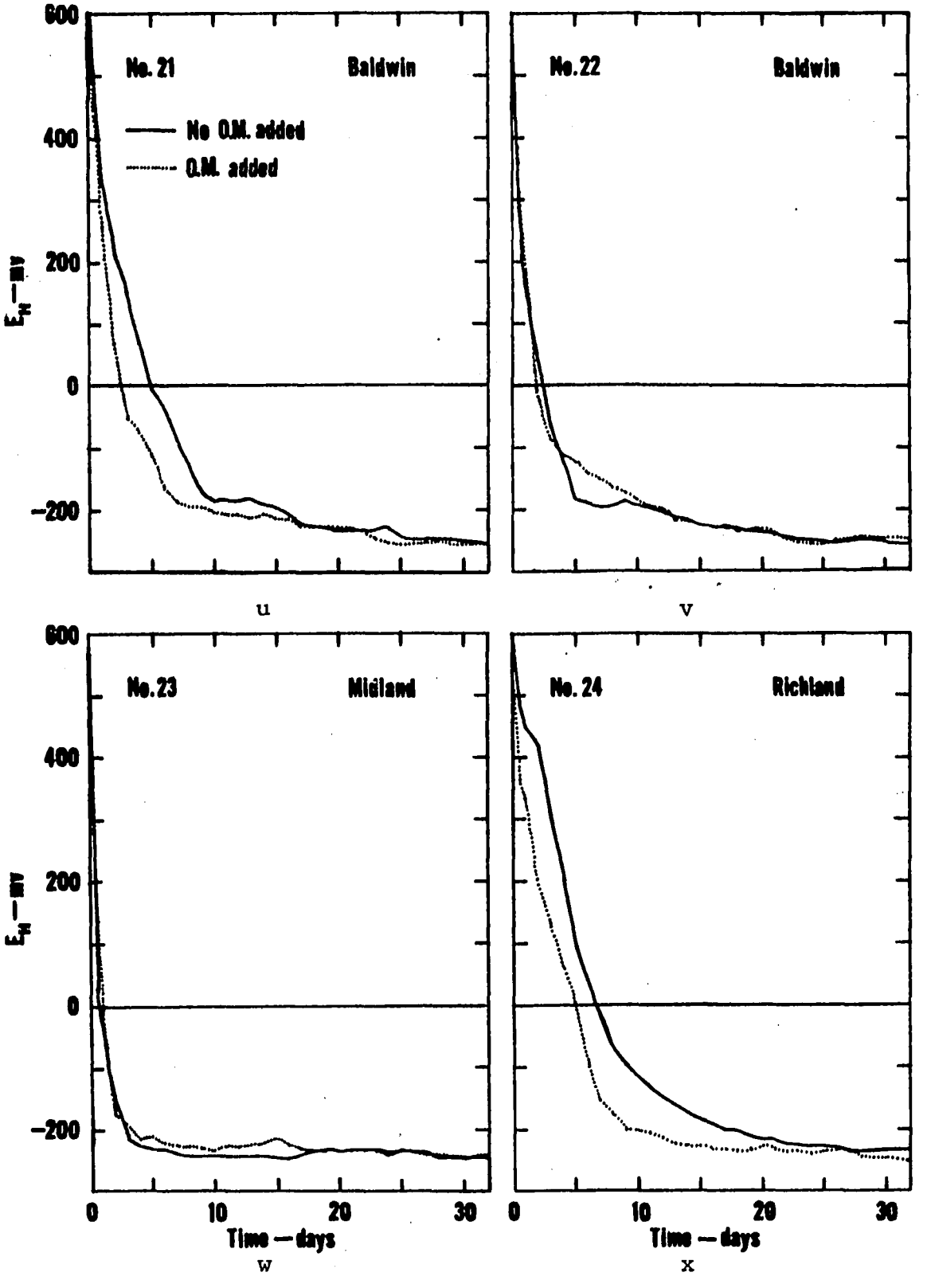
Figures 16i-161. Changes in redox potential after submergence with and without added organic matter.



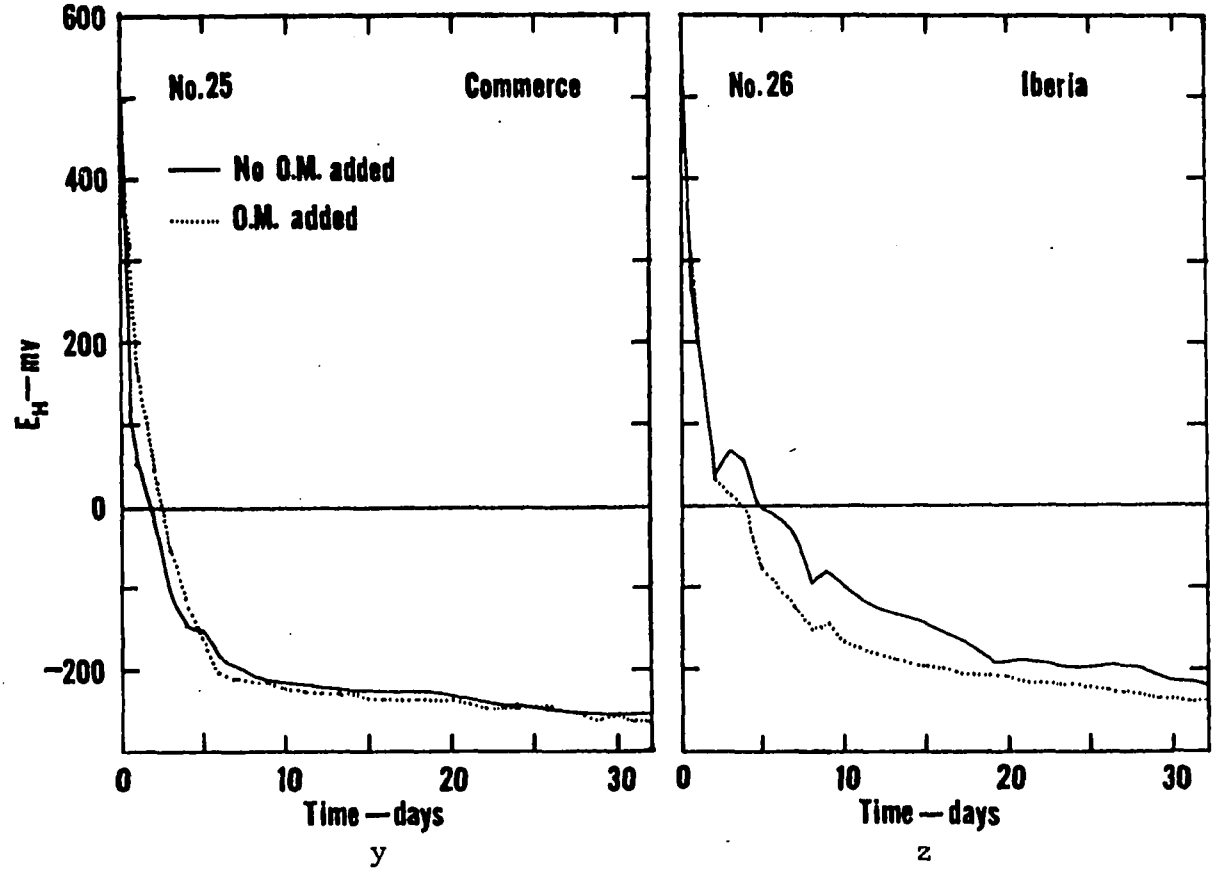
Figures 16m-16p. Changes in redox potential after submergence with and without added organic matter.



Figures 16q-16t. Changes in redox potential after submergence with and without added organic matter.



Figures 16u-16x. Changes in redox potential after submergence with and without added organic matter.



Figures 16y-16z. Changes in redox potential after submergence with and without added organic matter.

Table 11. Soil E_h as affected by submergence for 30 days with and without added organic matter (0.25% ground corn leaves).

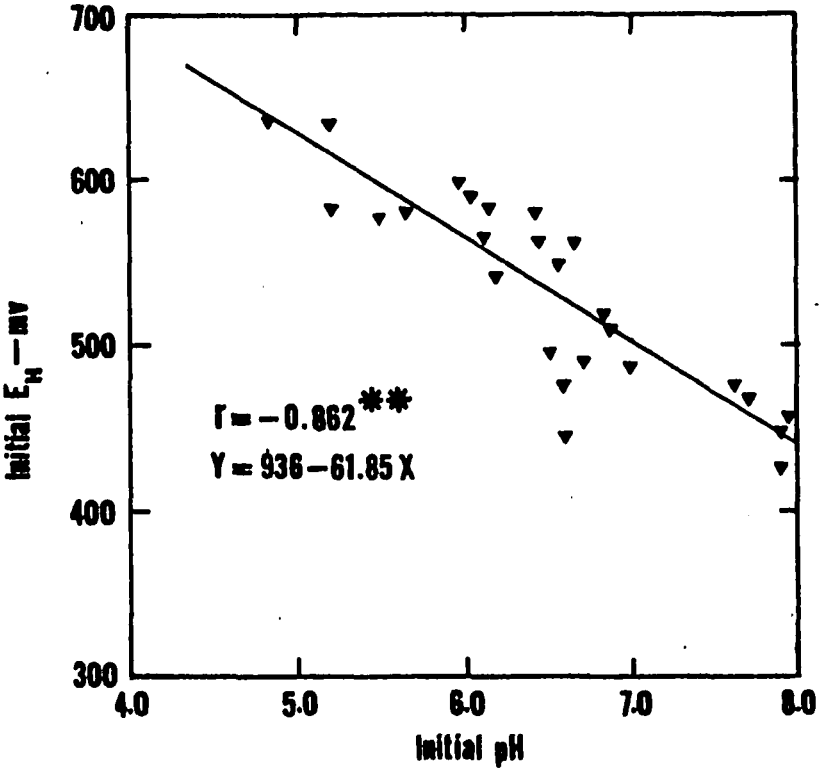
No.	Soil Type		E_h - millivolts					
			Initial[1]	Flooded with No. O.M. added	Flooded with O.M. added	Difference due to flooding	Difference due to flooding with O.M.	Difference due to added O.M.
1	Commerce	l	+519	-238	-238	+757	+757	0
2	Mhoon	sic	+562	-234	-254	+796	+816	+ 20
3	Commerce	l	+554	-236	-234	+790	+788	- 2
4	Mhoon	sicl	+474	-205	-241	+679	+715	+ 36
5	Sharkey	c	+444	-241	-246	+685	+690	+ 5
6	Richland	sil	+601	-239	-251	+840	+852	+ 12
7	Olivier	sil	+546	-238	-256	+784	+802	+ 18
8	Lintonia	sil	+589	-216	-234	+805	+823	+ 18
9	Gallion	sil	+569	-226	-228	+795	+797	+ 2
10	Yahola	sil	+461	-288	-251	+749	+712	- 37
11	Miller	sic	+476	-236	-284	+739	+760	+ 21
12	Yahola	sl	+424	-294	-291	+718	+715	- 3
13	Yahola	l	+444	-281	-276	+725	+720	- 5
14	Sharkey	cl	+492	- 94	-244	+586	+736	+150
15	Sharkey	sl	+477	-258	-268	+735	+745	+ 10
16	Sharkey	sic	+592	-244	-246	+836	+838	+ 2
17	Sharkey	l	+582	-226	-254	+808	+836	+ 28
18	Crowley	sil	+516	-284	-266	+800	+782	- 18
19	Baldwin	sicl	+634	-206	-223	+840	+857	+ 17
20	Mhoon	sicl	+491	-251	-254	+742	+745	+ 3
21	Baldwin	sicl	+634	-246	-253	+880	+887	+ 7
22	Baldwin	sicl	+579	-251	-246	+830	+825	- 5
23	Midland	sicl	+566	-244	-244	+810	+810	0
24	Richland	sil	+582	-236	-244	+818	+826	+ 8
25	Commerce	sl	+494	-254	-258	+748	+752	+ 4
26	Iberia	c	+579	-216	-234	+795	+813	+ 18

[1]Measured immediately after flooding with an excess of distilled water.

due to a temporary buildup of highly reducing organic compounds resulting from microbial activity. The temporary increase in potential probably resulted from these organic products being oxidized by iron and manganese compounds. Iron and manganese are effective in buffering the redox potential as noted in "Soil Chemistry" (1963), and as discussed elsewhere in this report. With an increase in time of submergence these soils became better poised, due to the higher concentration of reduced products, and the E_h values became less erratic. The potentials were observed to level off at values of E_h = -200 to -300 millivolts, Table 11.

With the addition of 0.25 per cent ground corn leaves the potentials decreased considerably faster, Figures 16a to 16z. Organic matter was usually effective in accelerating the reduction process. With the exception of the Sharkey clay loam (soil #14) organic matter did not significantly lower the final stable potential below the corresponding potential not receiving additional organic matter, Table 11. This particular soil had such a low organic matter content in relation to its texture that extremely high reducing conditions could not be obtained without the addition of an extra energy source. Organic matter added to this soil resulted in a greater reduction of iron and manganese as well as a lower redox potential than in the submerged sample not receiving organic matter.

There was a highly significant negative correlation (r = -0.564) between E_h and pH after 30 days submergence, Table 14. This data and its regression equation are plotted in Figure 18. An E_h/pH slope of -36 millivolts per pH unit was obtained. This is a considerably



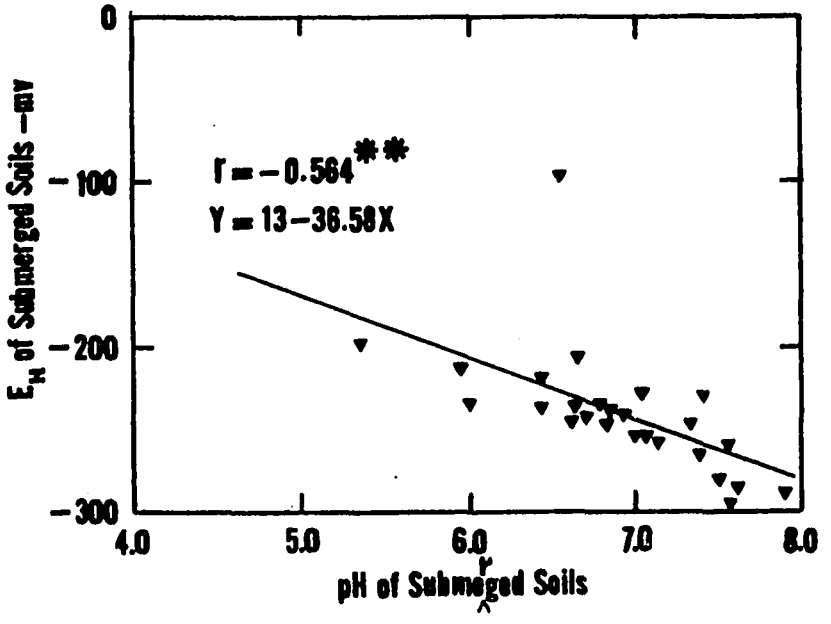


Figure 17. Relationship between redox potential and pH immediately after submergence.

Figure 18. Relationship between redox potential and pH of soils submerged 30 days.

lower slope than the -61.8 millivolts per pH unit slope which existed immediately after submergence of the soils. Slopes of the magnitude obtained in this study have recently been observed and have been attributed to the potential of bacterial cells, "Soil Chemistry", (1963).

The number of days required for the E_h to fall to a value of -200 millivolts was found to be positively significantly correlated with the ferrous iron concentration at 30 days, Figure 19. This indicates that the oxidized form of iron tended to maintain the potential at a high value until it was reduced to the ferrous form. The higher the amount of reducible ferric iron the greater the buffering effect of iron and the longer is required for the potential to fall to -200 millivolts. This suggests that the ferric-ferrous system is the dominant redox system in soils insofar as retarding the establishment of reduced conditions is concerned. The influence of manganese was not found significant although a tendency for manganese to retard reduction was noted.

Carbon Dioxide and Methane Production.

As shown in Table 12 the rate at which carbon dioxide was released during the mineralization of organic matter under waterlogged conditions varied with soil type, ranging from 3.5 to 109.5 cubic centimeters per 100 grams of air-dry soil (S.T.P.) for the Yahola sandy loam (soil #12) and the Iberia clay (soil #26), respectively. Figure 20 shows that carbon dioxide evolution increased with increasing clay content. Figure 22 shows that the magnitude of carbon dioxide evolution was also directly related to the organic matter content.

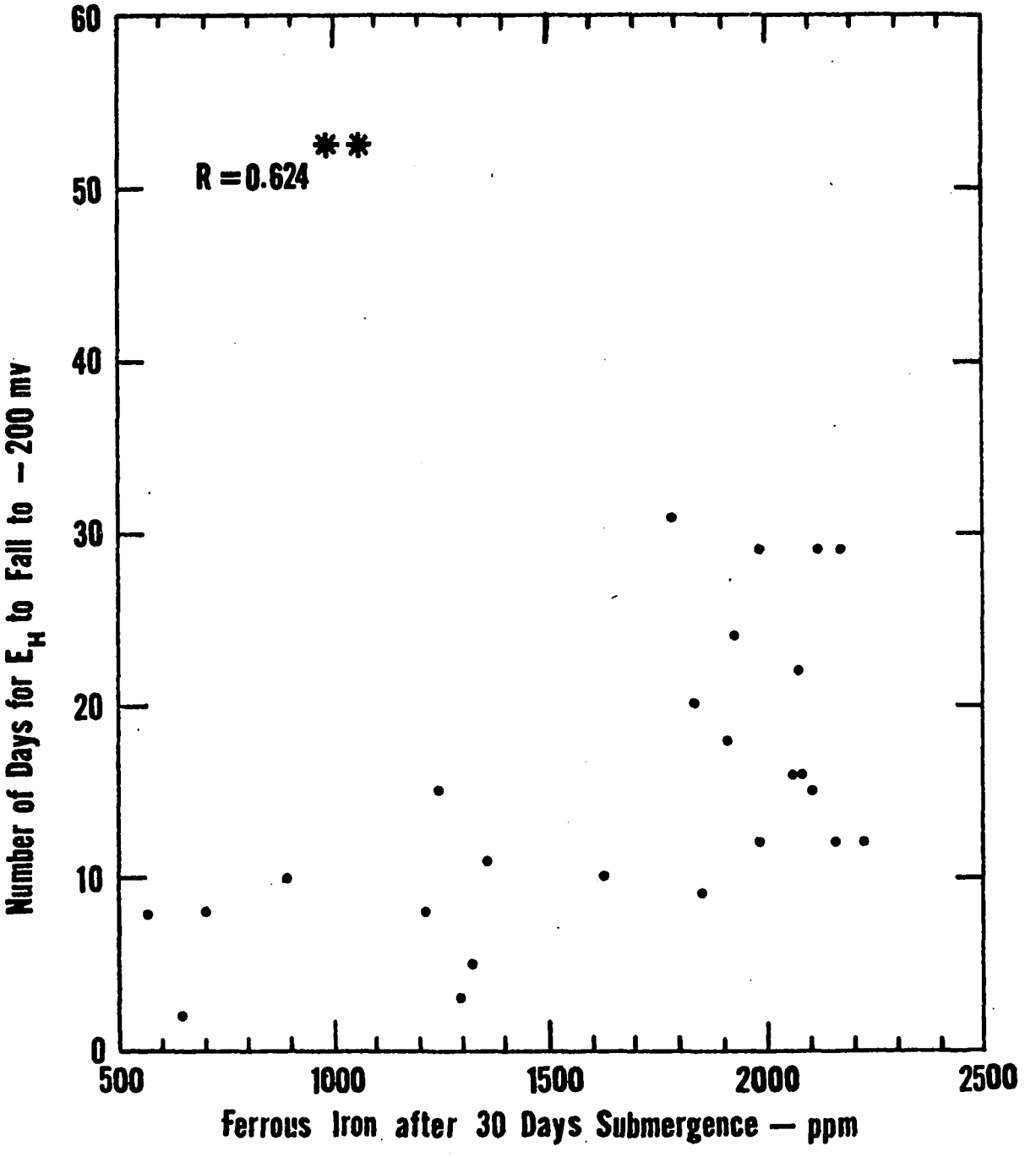


Figure 19. Relationship between time for redox potential to fall to -200 millivolts and ferrous iron content of soils submerged 30 days.

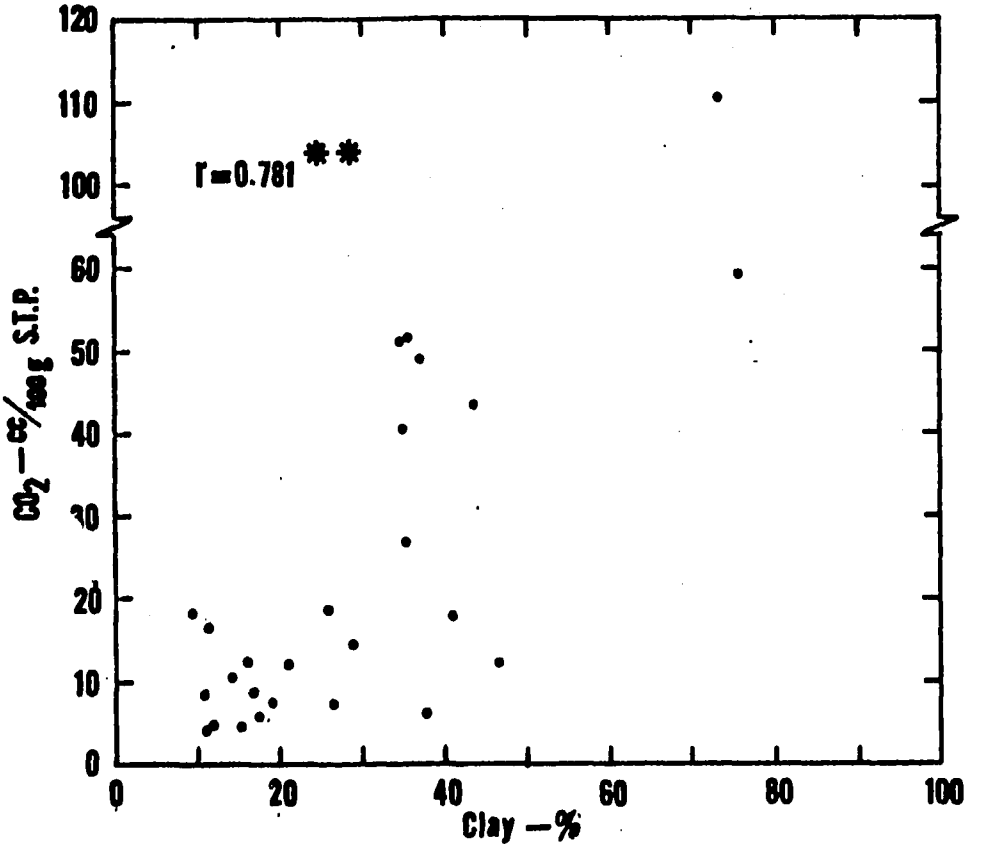
Table 12. Carbon dioxide and methane evolved as a result of water-logging for four and one-half months.

Sample No.	Soil Type		Cubic centimeters per 100 gms. of air-dry soil at S.T.P. CO_2	CH_4	CO_2-C/CH_4-C
1	Commerce	l	9.7	1.5	6.47
2	Mhoon	sic	42.5	31.4	1.35
3	Commerce	l	3.7	1.8	2.06
4	Mhoon	sicl	48.0	17.7	2.71
5	Sharkey	c	58.4	44.8	1.30
6	Richland	sil	6.7	0.7	9.57
7	Olivier	sil	11.2	5.4	2.07
8	Lintonia	sil	17.9	1.3	13.77
9	Gallion	sil	16.0	18.4	0.87
10	Yahola	sil	4.8	8.5	0.56
11	Miller	sic	11.1	5.3	2.09
12	Yahola	sl	3.5	5.6	0.62
13	Yahola	l	6.0	2.9	2.07
14	Sharkey	cl	26.0	0.3	86.67
15	Sharkey	sl	3.8	9.3	0.41
16	Sharkey	sic	16.7	8.7	1.92
17	Sharkey	l	8.2	2.2	3.73
18	Crowley	sil	7.4	6.4	1.16
19	Baldwin	sicl	13.5	6.5	2.08
20	Mhoon	sicl	50.5	25.2	2.00
21	Baldwin	sicl	50.6	34.9	1.45
22	Baldwin	sicl	40.0	23.1	1.73
23	Midland	sicl	5.0	3.6	1.39
24	Richland	sil	11.4	2.0	5.70
25	Commerce	sl	17.9	1.4	12.78
26	Iberia	c	109.5	61.2	1.79

The significant positive effects of clay and organic matter on carbon dioxide evolution were likely due to the fact that heavy-textured soils contained more organic matter, as has already been shown. The much greater microbial population of heavy clay soils also decomposed the organic matter more intensively with a greater evolution of carbon dioxide.

Under waterlogged conditions considerable methane was evolved during the decomposition of carbonaceous substrates. This is reflected by the data in Table 12 where methane production varied from 0.3 to 61.2 cubic centimeters per 100 grams of air-dry soil (S.T.P.) for the Sharkey clay loam (soil #14) and the Iberia clay (soil #26), respectively. Methane production was positively correlated with clay content, organic matter content, and carbon dioxide production as can be observed in Figures 21, 23, and 24. The production of methane was a consequence of incomplete metabolism of organic carbon under the low oxygen tensions of submerged soils. The biosynthesis of methane has been ascribed to special anaerobic methane-forming bacteria present in waterlogged soils. Clay soils which are subject to frequent periods of anaerobic conditions are likely to have a high population of specialized methane producing bacteria.

Generally, the carbon dioxide to methane ratios, tabulated in Table 12, show a greater evolution of carbon as carbon dioxide. The greater evolution of carbon as carbon dioxide than carbon as methane, for soils with ratios greater than 1.00, may be contributed to the fact that very large amounts of carbon dioxide were first produced when the soil was flooded, and before the evolution of methane commenced under highly reduced conditions.



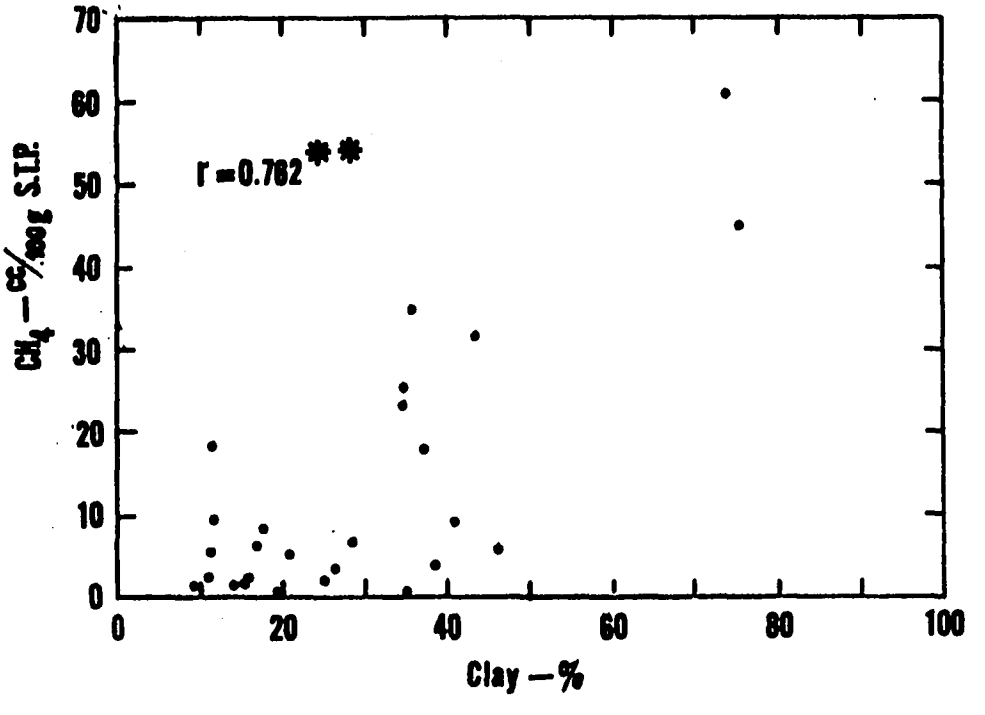
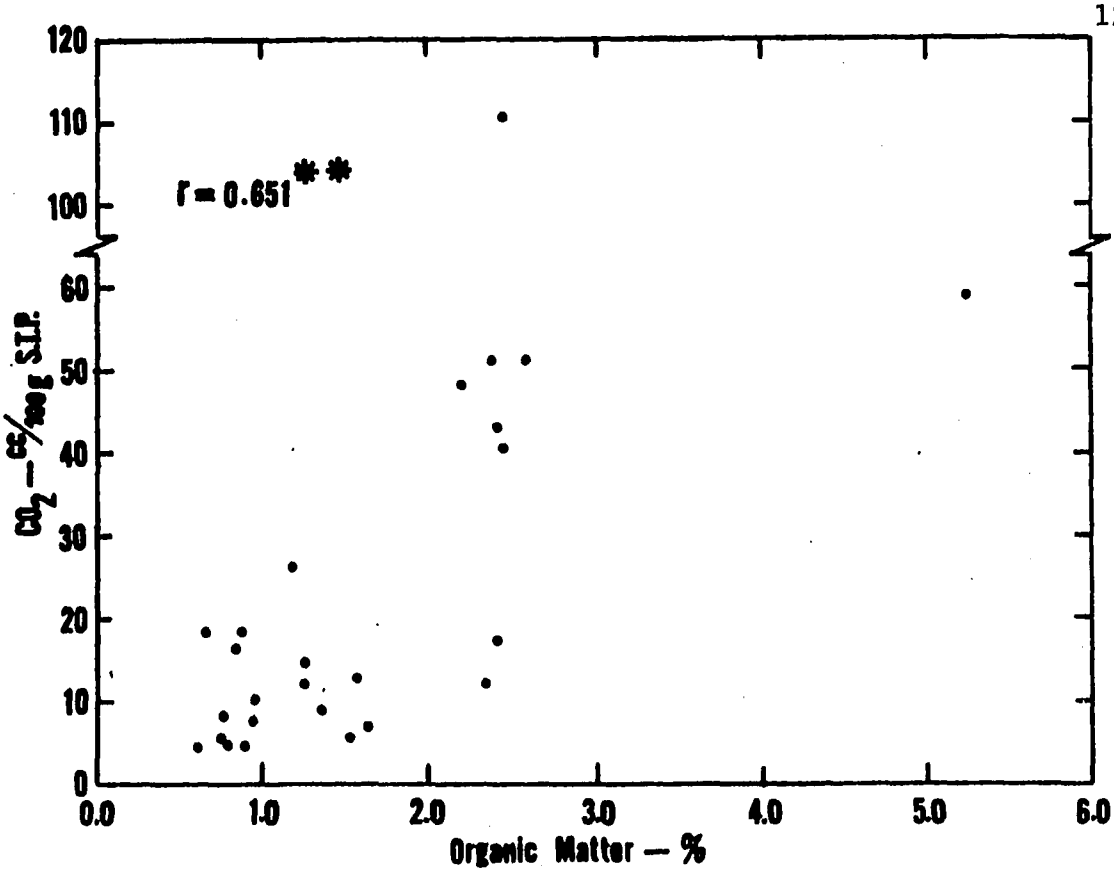


Figure 20. Correlation between carbon dioxide evolution in waterlogged soils and clay content.

Figure 21. Correlation between methane evolution in waterlogged soils and clay content.



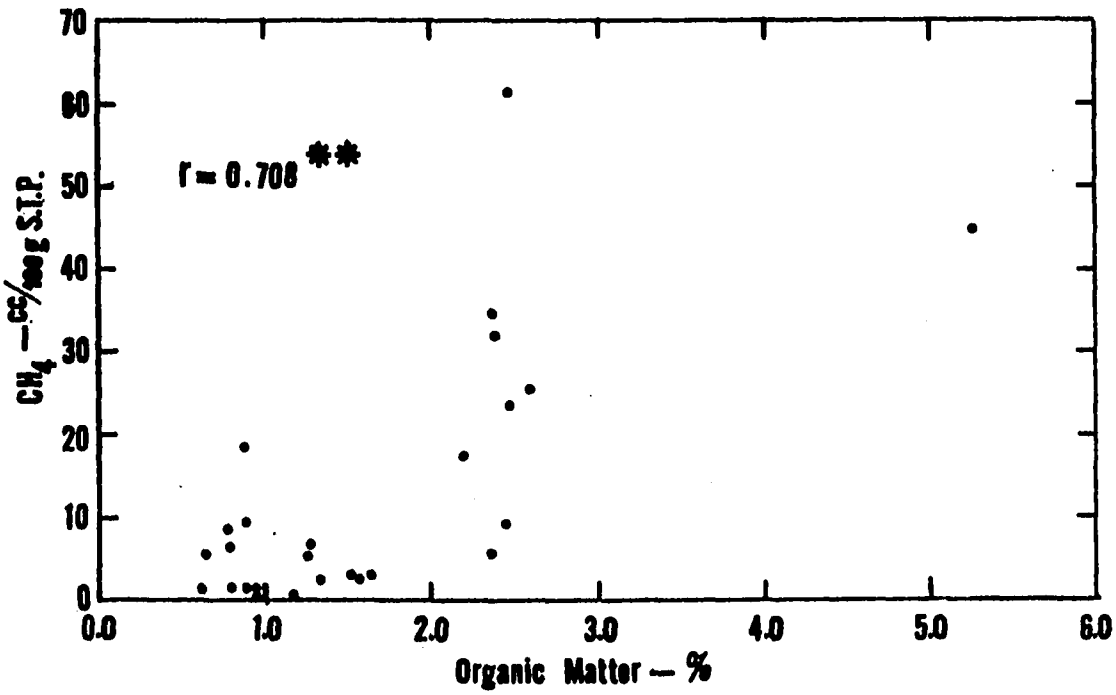


Figure 22. Correlation between carbon dioxide evolution in waterlogged soils and organic matter content.

Figure 23. Correlation between methane evolution in waterlogged soils and organic matter content.

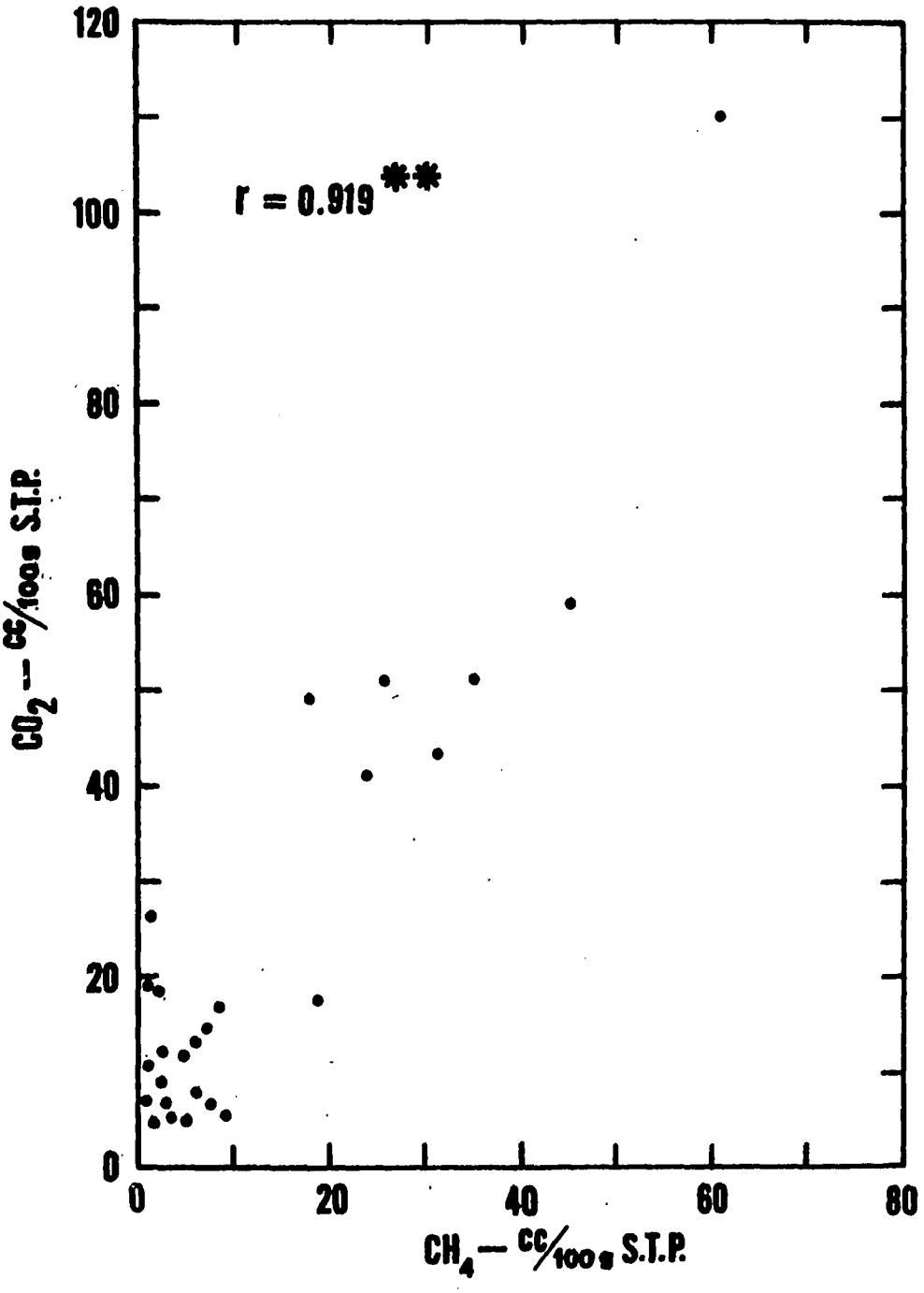


Figure 24. Correlation between carbon dioxide and methane evolutions in waterlogged soils.

Table 13. Simple correlation coefficient (r) among physical and chemical properties of 26 Louisiana soils before submergence.[1]

	O.M.	NH_4^+	NO_3^-	Fe^{++}	P	Mn	pH	L	Eh
Clay	.849	.466	-	.474	-	-	-	.739	-
O.M.		-	.462	.435	-	-	-	.823	-
NH_4^+			-	.511	-	-	-.604	-	.496
NO_3^-				-	-	-	-	.754	-
Fe^{++}					-	-	-.435	-	-
P						-	-	-	-.460
Mn							-	-	-
pH								-	-.862
L									-

[1] r at 5 per cent level of probability = 0.388.
r at 1 per cent level of probability = 0.496.

Table 14. Simple correlation coefficient (r) among physical, chemical and biological properties of 26 Louisiana soils after submergence.[1]

	O.M.	Nitrate Reduction (Quant.)	Nitrate Reduction (Qual.)	NH_4^+	Fe^{++}	P	Mn	pH	L	Eh	CO_2	CH_4
Clay	.849	.820	.546	.714	.625	-	-	-	.887	-	.781	.762
O.M.		.596	.627	.766	.674	.644	-	-	.918	-	.651	.708
Nitrate Reduction (Quant.)			.500	.574	.538	-	-	-.476	.662	-	.719	.722
Nitrate Reduction (Qual.)				.736	.474	.499	-	-	.677	-	.688	.717
NH_4^+					.668	.407	-	-	.798	-	.674	.733
Fe^{++}						-	.400	-.486	.671	-	.564	.494
P							-	-	.593	-	.432	.447
Mn								-	-	-	-	-
pH									-	-.564	-	-
L										-	.829	.774
Eh											-	-
CO_2												.919

[1] r at 5 per cent level of probability = 0.388.
r at 1 per cent level of probability = 0.496.

Table 15. Simple correlation coefficient (r) among physical and chemical properties before submergence and physical, chemical and biological properties after submergence for 26 Louisiana soils.[1]

	Before submergence							
	NH_4^+	NO_3^-	Fe^{++}	P	Mn	pH	L	Eh
Nitrate Reduction (Quant)	.663	-	.505	-	-	-.400	.569	-
Nitrate Reduction (Qual)	.409	-	.492	-	-	-	.544	-
NH_4^+	.522	-	.551	-	-	-.567	.528	-
Fe^{++}	.428	.405	-	-	.468	-.577	.556	.422
P	-	-	-	.908	-	-	.486	-
Mn	-	-	-	-	.755	-	-	-
pH	.604	-	-	-	-	.777	-	-.641
L	.387	-	.460	-	-	-	.774	-
E_h	-	-	-	-	-	-	-	-
CO_2	.631	-	.519	-	-	-.441	.547	-
CH_4	.580	-	.586	-	-	-	.568	-

[1]r at 5 per cent level of probability = 0.388.
r at 1 per cent level of probability = 0.496.

The mass spectrometer analysis also revealed the presence of nitrogen gas, oxygen, water vapor and argon which are natural constituents of the atmosphere. Analysis of hydrogen was not made. Carbon dioxide and methane accounted for most of the gases.

SUMMARY AND CONCLUSIONS

A study has been made of the effects of submergence on denitrification and physicochemical properties of 26 Louisiana soils.

Flooding moist soils with a solution containing nitrate nitrogen and periodically analyzing for nitrates indicated a reduction of nitrate with time. Nitrate reduction rates were calculated for each of the 26 soils studied without the addition of organic matter. These reduction rates were positively correlated with clay, organic matter, and carbon dioxide and methane evolution. With the addition of organic matter, in the form of 0.25 per cent ground corn leaves, the nitrate reduction rates were almost invariably increased with each sample responding differently to the added organic matter.

In a second experiment on nitrate reduction, nitrate reduction rates were estimated by adding nitrate to submerged anaerobic soils and measuring nitrate qualitatively to determine how long it required the soil to reduce the nitrate. The results obtained by this second method differed in some respects but were in general agreement with the results of the first experiment.

Nitrogen gas was the only gaseous product of denitrification, in appreciable quantity, detected by mass spectrometer analysis after adding nitrate nitrogen to highly reduced and waterlogged soils. Recovery of the added nitrate as nitrogen gas ranged from 0.3 per cent to 80.0 per cent. No nitrate was detected in the soil at the time of

gas analysis. Obviously, part, and in some cases almost all, of the added nitrate was present as intermediate products.

Flooding markedly increased the ammonia content of the soils. There was a highly significant positive correlation between organic matter content before flooding and the ammonia content 30 days after flooding. Under submerged conditions the mineralization of nitrogen stopped at the ammonia stage. With the addition of 0.25 per cent ground corn leaves flooding caused an even greater increase in ammonia. The added organic nitrogen was mineralized to different extents in different soils. The mineralization of some nitrogen from the organic matter initially present appears to have been stimulated by the added organic material.

Submergence caused very large increases in iron which were positively correlated with clay and organic matter contents. This relationship was due to the greater reduction of oxidized forms of iron by microorganisms and by reduced products of microbial activity as shown by the correlations of ferrous iron with carbon dioxide and methane evolution. Ferrous iron represented nearly all the extractable iron 30 days after submergence. The concentrations of ferrous iron after 30 days submergence were not statistically higher where organic matter was added, although there was an indication of this effect. The more acid soils had larger ferrous iron concentrations under submergence due to the fact that these acid soils are usually higher in iron oxide. No correlation existed between the ferrous iron contents before flooding and after flooding.

Flooding generally increased the amount of extractable phosphorus. There was an average increase of 21 per cent in extractable phosphorus after submergence for 30 days. The amount of phosphorus released was affected by the organic matter content of the soil. The reduction of ferric phosphate to the more soluble ferrous phosphate obviously contributed to increases in extractable phosphorus in submerged soils.

Extractable manganese concentrations were increased after flooding and these concentrations were related to the manganese concentrations before flooding. There was an average six-fold increase in extractable manganese upon submergence. Similarly to ferric compounds, manganic compounds, acting as electron acceptors, were probably reduced both biologically, and chemically. The effect of adding organic matter was inconsistent although there was a tendency for an increase in manganese to result from organic matter addition. Since manganese is so readily reduced it is likely that organic matter in addition to that already present in the soil is not necessary for manganese release under submerged conditions.

Flooding for 30 days generally increased the pH of those soils with initial pH values below 7.4 and decrease the pH of soils with initial pH values above 7.4. The average increase or decrease was 0.53 pH unit for each pH unit below or above pH 7.4. The results showed that the greatest increases in pH can be expected from soils with a lower initial pH. Organic matter generally favored the development of a higher pH after 30 days submergence. Increases in pH were considered due to hydrolysis of minerals and reduction processes while

decreases were attributed to organic acids produced during anaerobic fermentation, and to dissolved carbon dioxide. There was a tendency for the pH of submerged soils to be buffered around neutrality, with ferrous carbonate possibly playing an important role.

Specific conductivity generally increased upon submerging the soils. This increase was highly correlated with clay, organic matter, ammonia, ferrous iron and phosphorus contents and with carbon dioxide production and methane production. Drops in specific conductance after submergence were associated with soils which were initially very high in nitrate nitrogen.

There was a close inverse relationship between E_h immediately after submergence and the pH of the soil. The E_h/pH slope was -61.8 millivolts per pH unit. Submergence caused a sharp drop in potential. Potentials after 32 days flooding were observed to level off at -200 to -300 millivolts, except for the Sharkey clay loam (soil #14). This was attributed to its rather low organic matter content in relation to its texture. The addition of organic matter caused a faster drop in potential. There was also a close inverse relationship between E_h and pH after 30 days submergence. The E_h/pH slope was -36.6 millivolts per pH unit. The higher the reducible ferric iron content the longer it required to become highly reducing (-200 millivolts).

Methane and carbon dioxide evolutions were the main gaseous products of waterlogged soils. Methane and carbon dioxide were positively correlated with each other, and with the organic matter and clay contents of the soils.

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AUTOBIOGRAPHY

Francis Hamilton Redman was born June 21, 1933 at San Pedro de Macoris, Dominican Republic. He received his elementary education in the Dominican Republic and Barbados, and high school training in Barbados, W. I.

He entered Macdonald College of McGill University, in Montreal Canada, in September, 1952 and graduated in May, 1956.

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Major Field: Agronomy

Title of Thesis: Effect of Submergence of Denitrification and Physicochemical Properties of Important Louisiana Soils

Approved:

Wm. H. Patrick, Jr.
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